Photochemistry of Cyclic Enones. Part 8.[1] 5-(But-3-enyl)-3-phenylcyclopent-2-enone and 5-(Pent-4-enyl)-3-phenylcyclopent-2-enone

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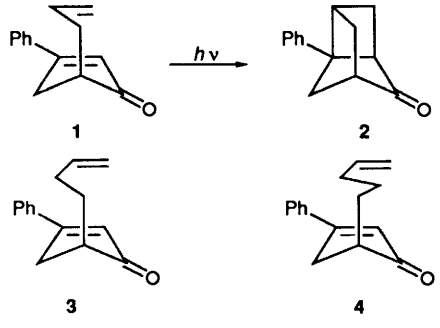
Photolysis of 5-(but-3-enyl)-3-phenylcyclopent-2-enone in benzene solution using a Pyrex filter affords two products in the ratio 2:1. These are 1-phenyltricyclo[4.2.1.$0^{3,8}$]nonan-7-one and 8-phenyltricyclo[4.2.1.$0^{3,8}$]nonan-9-one. They are inseparable by column chromatography, but their structure follows from examination of the four separable lactones derived from the mixture by Baeyer–Villiger oxidation.

Photolysis of 5-(pent-4-enyl)-3-phenylcyclopent-2-enone under the same conditions affords only one product, 9-phenyltricyclo[5.2.1.$0^{3,9}$]decan-10-one, whose structure follows from examination of the two lactones derived by similar oxidation.

These results demonstrate that in these compounds the regioselectivity of ring closure depends on the length of the 5-side-chain.

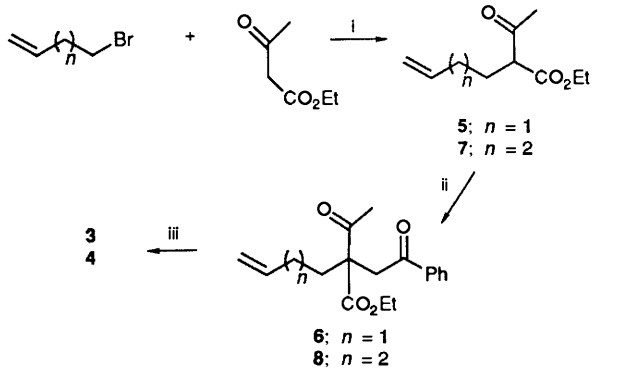
We have recently examined a number of examples of the photolysis of 5-allylcyclopent-2-enones[2–4] (*e.g.* **1**) (see also ref. 5). In all these cases, the regioselectivity is such that we have only been able to isolate one product, which has the structure **2**. We wished to explore the effect of a change of the length of the side-chain on the regioselectivity of the reaction, and this paper describes the synthesis and photochemistry of 5-(but-3-enyl)-3-phenylcyclopent-2-enone **3** and 5-(pent-4-enyl)-3-phenylcyclopent-2-enone **4**.



Synthesis.—We employed the general synthetic strategy that we had employed in earlier papers. Alkylation of ethyl acetoacetate with 4-bromobut-1-ene afforded the keto ester **5**.[6] Alkylation of compound **5** with phenacyl bromide gave the diketo ester **6**, which was hydrolysed, decarboxylated, and cyclised to give compound **3**. In a similar manner, alkylation of ethyl acetoacetate with 5-bromopent-1-ene[7] afforded the keto ester **7**[6] which was converted into the diketo ester **8**. This in turn afforded the cyclopentenone **4** (Scheme 1).

Photolysis Experiments.—When we photolysed the butenyl ketone **3**, two monomeric photoproducts were obtained as well as a dimer. The quantity of dimer could be reduced by carrying out the photolysis in more dilute solution. The two monomeric photoproducts were obtained in 49% yield in the ratio 2:1 after 35 min, but on further photolysis (12 h), the ratio changed to 19:1. Clearly, the minor isomer underwent further photolysis though we were unable to identify any product from this secondary reaction. No enol ether or aldehyde related to this compound, of the types obtained as further photolysis products in our earlier work, could be detected.

The two monomeric photoproducts could be separated from

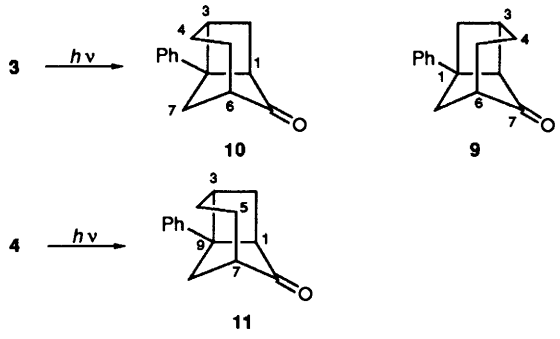


Scheme 1 *Reagents:* i, NaH, DME; ii, $BrCH_2COPh$; iii, 1% KOH followed by 10% KOH

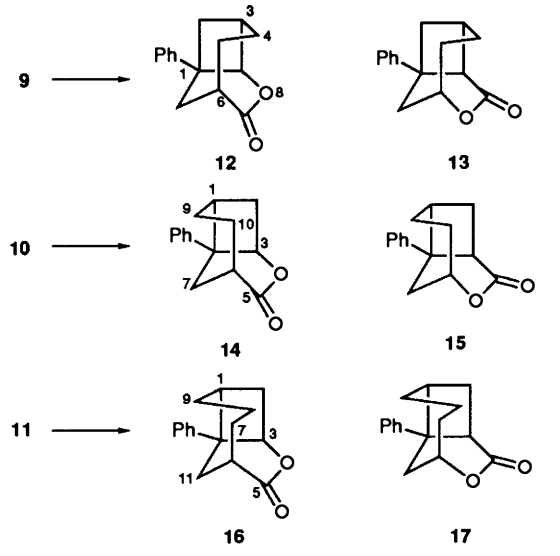
starting material, but not from the photodimer, by chromatography. The mixture of the three photoproducts on distillation gave the two monomeric products and the starting enone, the latter being formed from pyrolysis of the photodimer. The enone could then be removed by further chromatography but the two monomeric cage ketones could not be separated. However, we were able to analyse the mixture by GC-MS and to assign ^{13}C NMR spectra.

The structure of the two ketones **9** and **10** was confirmed by carrying out a Baeyer–Villiger oxidation on the mixture, using the method described by Kametani.[8] The resulting mixture, on chromatography, could be separated into a mixture of starting ketones, and four lactones. In the oxidation the proportion of the major ketone increases in the recovered, unchanged starting material, suggesting that the minor isomer is oxidised in preference to the major product.

All the lactones show peaks in their ^1H NMR spectrum at δ *ca.* 5, characteristic of the CHOCO proton signal and at δ 3.0–3.5, characteristic of the $CHCO_2$ proton signal. One of the lactones shows the simplest signal characteristic of a CHOCO system—a doublet (J 7.8 Hz) at δ_H 5.08. The lactone must be compound **12**. Similarly, another lactone shows a doublet at δ 3.56, indicating that it has the structure **13**. Of the other two lactones, the CHOCO peak is a double triplet in one, and the $CHCO_2$ peak is a double double doublet in the other. This suggests that these two lactones have structure **14** and **15** respectively. In both these lactones, the 3-proton would be



coupled to the 2-*endo*-proton, the 2-*exo*-proton, and the 1-proton. The 6-proton signal would be more complex in these two cases and is in fact a dtd or dddd, respectively.



The two lactones **12** and **13** must be derived from the ketone **9** while the isomers **14** and **15** are derived from its isomer **10**. Taking into account the recovered starting material—with its change in ketone ratio—the quantities of products **12** and **13** isolated are too large to be derived from the minor ketone. Hence the ketone **9** is the major photoproduct, and compound **10** the minor product. The major product **9** has the more hindered carbonyl group, and hence should react more slowly with peracid. The minor isomer **10** undergoes further photolysis, as does its homologue **2**, though we were unable to identify the products formed from ketone **10**.

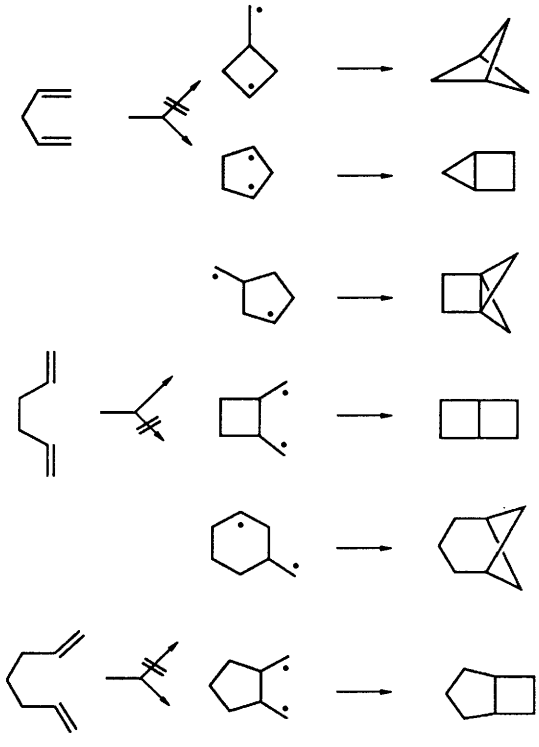
There is one more distinction between compounds **9** and **10** that needs to be mentioned. The mass spectrum of the minor isomer **10** is almost identical with that of the butenylcyclopentenone **3**, while that of the major isomer **9** shows distinct differences. This suggests that compound **10** is reconverted into compound **3** under mass spectrometer (EI) conditions. This probably involves a mechanism where an electron is ejected from the phenyl ring rather than the carbonyl group. It is interesting that similar behaviour is shown by compounds of type **2**, and by the tricycle **11** (see below).

Photolysis of the higher homologue **4** affords only one product, compound **11**, in 58% yield. The structure of this compound follows from examination of the two Baeyer–Villiger lactones (**16** and **17**). In one of these, the ^{1}H NMR spectrum shows peaks at δ 5.28 as a double double doublet, and a more complex signal at δ 3.02. In the other it is the peak at δ 3.55 which is the double double doublet, while the peak at δ 5.97 is more complex. Again the 3-proton is coupled to the two 2-protons and to the 1-proton.

Discussion

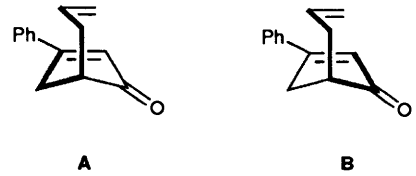
We now have to address the problem of regioselectivity in these reactions. Photochemical cycloaddition reactions of enes to enones, including intramolecular examples, have been reviewed very recently.[9] Srinivasan[10] and Hammond[11] have both suggested that the regiochemistry of intramolecular reactions could be explained 'on the basis of "rule of five", which was justified by entropy factors.' This 'rule of five' stated that any reaction will be favoured if it involves an intermediate diradical associated with a five-membered ring. Gleiter[12] suggested that the explanation for the 'rule of five' lay in the interplay of 'through space' and 'through bond' frontier orbital interactions. Ohsaku[13] supported this approach with further calculations.

Gleiter[12] formulated the rule in a different way, and pointed out that the regiochemistry of many of the photochemical intramolecular cycloaddition reactions of two enes was controlled by the number of atoms comprising the chain which links the two enes. Where this number was even, cross-cycloaddition takes place; while if it is odd, parallel cycloaddition occurs (Scheme 2).



Scheme 2

When we tried to apply the Gleiter treatment to the cases which we have already reported[2–4] and to the cases described in this paper, a problem arose. For the 5-allylcyclopentenone case, there are two possible pathways between the side-chain double bond and the ring double bond. The first of these (**A**) involves the allylic aliphatic methylene group, and the 5- and 4-carbon of the ring: the second (**B**) involves the allylic aliphatic



A **B**

methylene group, and the 5- and 1-carbon of the ring. We can accommodate all our results with Gleiter's formulation[12] if we involve pathway A and *rule out the pathway involving the carbonyl group*. Thus, in compounds **1** and **4**, there are three and five bonds, respectively, and parallel cycloaddition occurs to give products **2** and **11**. In compound **3** there are four carbon atoms between the termini, and the major product is tricycle **9**. In most cases, where the same ambiguity exists, our hypothesis explains the results, though a few exceptions exist. These include some of the results reported in Agosta's papers;[14–16] others appear in papers by Pattenden,[17] and Tamura *et al.*[18,19]

Most of these exceptions involve molecules where there are substituents either on the ene or on the enone. Gleiter's treatment ignores substituents, which undoubtedly have an effect on the regiochemistry of these cycloadditions, and, indeed, Agosta's papers[14–16] have been dedicated to exploring the effect of substituents on regioselectivity. Gleiter, too, has recently reported[20] on how substituents change the regioselectivity in the intramolecular cases of methoxyenes with cyclohexenones.

We have shown already[1] that cycloaddition of 5-allyl-3-phenylcyclopent-2-enone proceeds *via* a triplet excited state, and there is no doubt that the compounds described here must involve triplet states, too. It has been envisaged that the next step involves an exciplex formed between triplet enone and ground-state ene. However, Turro and Schuster[21] have recently cast doubt on the necessity for the intermediacy of exciplexes in at least some intermolecular cycloaddition reactions. The exciplex, if it exists, collapses to a diradical, which then either gives product or returns to starting material.

Experimental

Procedure.—For general instructions see Part 6.[5] NMR spectra were measured in deuteriochloroform solution, with $SiMe_4$ as internal standard, on either a Bruker WP80, Jeol GX270, or a Varian XL200 machine. *J*-values are given in Hz. Photolyses were carried out in benzene solution using a Pyrex filter with a Hanovia 450W medium-pressure lamp. IR spectra of liquids were measured as films, and those of solids as Nujol mulls. UV spectra were measured in ethanol solution using a Pye Unicam PU 880 spectrophotometer.

Ethyl 2-Acetylhex-5-enoate **5**.—A solution of ethyl 3-oxobutanoate (30.5 g, 0.23 mol) in 1,2-dimethoxyethane (DME) (75 cm^3) was added dropwise under nitrogen to a stirred mixture of sodium hydride (4.63 g, 0.19 mol; previously washed with hexane) in DME (75 cm^3). When evolution of hydrogen had ceased a solution of 4-bromobut-1-ene (26.3 g, 0.19 mol) in DME (100 cm^3) was added dropwise to the stirred mixture. The mixture was then heated under reflux for 23 h. The solvent was removed by distillation and the residue was diluted with water (100 cm^3) and extracted with diethyl ether (6 × 80 cm^3). The combined organic layers were washed with water (100 cm^3), dried ($MgSO_4$), and concentrated. Distillation of the residue afforded the starting ester (4.0 g recovery), b.p. 70–75 °C/10 mmHg and ethyl 2-acetylhex-5-enoate **5** (27.9 g, 79%), b.p. 84–88 °C/10 mmHg (lit.,[6] 65%; b.p. 103–110 °C/22 mmHg); ν_{max}/cm^{-1} 1740 (CO, ester), 1715 (CO, acyl) and 1640 (C=C); δ_H 1.08 (t, *J* 6, ester Me), 1.62–1.65 (m, 3-H), 1.93 (s, MeCO), 3.17 (t, $J_{2,3}$ 7, 2-H), 3.90 (q, *J* 6, ester CH_2), 4.86 (d further split, $J_{6cis,5}$ 11, 6-H^a) and 4.88 (d further split, $J_{6trans,5}$ 15, $J_{5,6cis}$ 11, and $J_{5,4}$ 7, 5-H).

Ethyl 2-Acetyl-2-phenacylhex-5-enoate **6**.—A solution of the keto ester **5** (5.0 g, 27.2 mmol) in DME (50 cm^3) was added dropwise under nitrogen to a stirred mixture of sodium hydride (0.65 g, 27.2 mmol; previously washed with hexane) in DME (100 cm^3). The mixture was heated to 50–60 °C for 30 min, and then cooled on ice. A solution of phenacyl bromide (5.41 g, 27.2 mmol) in DME (70 cm^3) was then added dropwise to the mixture, stirred at 0 °C. After the addition was complete, the mixture was stirred at 0 °C for 1.5 h, allowed to warm to room temperature, and stirred for 30 min. The solvent was removed by distillation and the residue was extracted with diethyl ether (3 × 70 cm^3). The combined organic layers were washed with water (100 cm^3) and dried ($MgSO_4$). Removal of the solvent afforded ethyl 2-acetyl-2-phenacylhex-5-enoate **6** as an oil, which was purified by flash chromatography (4.25 g, 52%); ν_{max}/cm^{-1} 1755 (CO, ester), 1710 (CO, acyl), 1685 (CO, phenacyl) and 1640 (C=C); δ_H 1.23 (t, *J* 8, ester Me), 1.88–2.26 (m, 3- and 4-H_2), 2.38 (s, MeCO), 3.69 (s, PhCOCH_2), 4.16 (q, *J* 8, ester CH_2), 4.96 (d further split, $J_{6cis,5}$ 11, 6-H^a), 5.03 (d further split, $J_{6trans,5}$ 17, 6-H^b), 5.70 (ddt, $J_{5,6cis}$ 17, $J_{5,6trans}$ 11 and $J_{5,4}$ 7, 5-H) and 7.26–7.91 (m, ArH).

5-(*But*-3-*enyl*)-3-*phenylcyclopent*-2-*enone* **3**.—The diketo ester **6** (7.57 g, 25.1 mmol) was heated under reflux for 2 h, under a flow of nitrogen, in aq. potassium hydroxide (0.31 mol dm^{-3}; 620 cm^3), which had been previously boiled to remove dissolved oxygen. The basicity of the reaction mixture was then increased by the addition of further aq. potassium hydroxide (2.67 mol dm^{-3}; 500 cm^3). The mixture was heated under reflux for 1.5 h. After cooling, the mixture was neutralised by the addition of conc. sulphuric acid, and extracted with diethyl ether (6 × 150 cm^3). The extract was washed with water (3 × 150 cm^3), dried ($MgSO_4$) and evaporated to give 5-(*but*-3-*enyl*)-3-*phenylcyclopent*-2-*enone* **3** as a yellow oil, which was purified by distillation (3.82 g, 72%), b.p. 124–125 °C/0.12 mmHg (Found: C, 84.8; H, 7.7. $C_{15}H_{16}O$ requires C, 84.87; H, 7.60%); ν_{max}/cm^{-1} 1690 (CO); λ_{max}(EtOH)/nm 285 (log ε 4.23); δ_H 1.25–1.93 (m, butene 1-H_2), 2.03–2.25 (m, butene 2-H_2), 2.43–2.73 (m, 4-H_{trans} and 5-H), 3.10 (ddd, J_{gem} 18, $J_{4,5}$ 9, and $J_{4,2}$ 2, 4-H_{cis}), 4.97 (d further split, $J_{4cis,CH=CH_2}$ 10, CH=C*H*^{a}H), 5.02 (d further split, $J_{4trans,CH=CH_2}$ 18, CH=CH*H*^{b}), 5.97 (ddt, $J_{3,4\text{-}trans\text{-butenyl}}$ 18, $J_{3,4\text{-}cis\text{-butenyl}}$ 10, and $J_{3,2\text{-butenyl}}$ 7, C*H*=CH$_2$), 6.47 (t, $J_{2,4}$ 2, 2-H) and 7.31–7.65 (m, ArH); δ_C 30.9 (t, butene C-1), 31.5 (t, butene C-2), 35.5 (t, C-4), 45.7 (d, C-5), 115.3 (t, butene C-4), 126.9 and 127.1 (ArC and C-2), 129.0, 131.2 and 134.3 (ArC), 138.0 (d, butene C-3), 172.1 (s, C-3) and 210.8 (s, C-1); *m/z* 212 (M$^+$, 3%), 158 (100), 128 (55) and 115 (62).

Ethyl 2-Acetylhept-6-enoate **7**.[6]—A solution of ethyl 3-oxobutanoate (8.38 g, 64.4 mmol) in DME (75 cm^3) was added dropwise under nitrogen to a stirred mixture of sodium hydride (1.29 g, 53.7 mmol; previously washed with hexane) in DME (100 cm^3). When evolution of hydrogen had ceased, a solution of 5-bromopent-1-ene (8.00 g, 53.7 mmol) in DME (75 cm^3) was added dropwise to the stirred mixture, which was then heated under reflux for 20 h. The solvent was removed by distillation, and the residue was diluted with water (100 cm^3) and extracted with diethyl ether (5 × 100 cm^3). The combined extracts were washed with water (100 cm^3), dried ($MgSO_4$), and concentrated. Distillation of the residue afforded ethyl 3-oxobutanoate (0.31 g recovery), b.p. 30–34 °C/1.2 mmHg, and ethyl 2-acetylhept-6-enoate **7** (8.93 g, 84%), b.p. 60–62 °C/1.2 mmHg (lit.,[6] 73%; b.p. 69–72 °C/2 mmHg); ν_{max}/cm^{-1} 1740 (CO, ester), 1715 (CO, acyl) and 1640 (C=C); δ_H 1.18 (t, *J* 7, ester Me), 1.66–2.19 (m, 3-, 4- and 5-H_2), 2.12 (s, MeCO), 3.32 (t, $J_{2,3}$ 7, 2-H), 4.11 (q, *J* 7, ester CH_2), 4.87 (d further split, $J_{7cis,6}$ 11, 7-H^a), 4.91 (d further split, $J_{7trans,6}$ 15, 7-H^b) and 5.07 (ddt, $J_{6,7trans}$ 15, $J_{6,7cis}$ 11, and $J_{6,5}$ 6, 6-H).

Ethyl 2-Acetyl-2-phenacylhept-6-enoate **8**.—A solution of the above keto ester **7** (11.16 g, 56.4 mmol) in DME (70 cm^3) was

added dropwise under nitrogen to a stirred mixture of sodium hydride (1.35 g, 56.4 mmol; previously washed with hexane) in DME (100 cm^3). The mixture was then heated to 50–60 °C for 130 min, and then cooled on ice. A solution of phenacyl bromide (11.22 g, 56.4 mmol) in DME (100 cm^3) was added dropwise to the mixture, which was then stirred at 0 °C for 1 h, and at room temperature for a further 2.5 h. The solvent was removed by distillation, and the residue was diluted with water (100 cm^3) and extracted with diethyl ether (4 × 70 cm^3). The combined extracts were washed with water (100 cm^3), dried ($MgSO_4$) and concentrated. The residue was purified by flash chromatography to yield ethyl 2-acetyl-2-phenacylhept-6-enoate **8** as a viscous orange oil (8.50 g, 48%); ν_{max}/cm^{-1} 1730 (CO, ester), 1710 (CO, acyl), 1690 (CO, phenacyl) and 1590 (C=C); δ_H 1.14 (t, *J* 7, ester Me), 1.82–2.13 (m, 3-, 4- and 5-H_2), 2.31 (s, MeCO), 3.62 (s, PhCOCH_2), 4.13 (q, *J* 7, ester CH_2), 4.88 (d further split, $J_{7cis,6}$ 11, 7-H^a), 4.01 (d further split, $J_{7trans,6}$ 17, 7-H^b), 5.64 (ddt, $J_{6,7trans}$ 17, $J_{6,7cis}$ 11, and $J_{6,5}$ 7, 6-H) and 7.27–8.05 (m, ArH).

5-(*Pent*-4-*enyl*)-3-*phenylcyclopent*-2-*enone* **4**.—The diketo ester **8** (8.50 g, 26.9 mmol) was heated under reflux for 2 h under nitrogen in aq. potassium hydroxide (0.31 mol dm^{-3}; 670 cm^3) which had been previously boiled to remove dissolved oxygen. The basicity of the reaction mixture was then increased by the addition of further aq. potassium hydroxide (2.67 mol dm^{-3}; 600 cm^3). The mixture was heated under reflux for a further 2 h. After cooling, the mixture was neutralised by the addition of conc. sulphuric acid, and extracted with diethyl ether (5 × 100 cm^3). The combined extracts were washed with water (3 × 100 cm^3) and dried ($MgSO_4$), and removal of the solvent by distillation gave a crude product, which was distilled to yield 5-(*pent*-4-*enyl*)-3-*phenylcyclopent*-2-*enone* **4** (3.50 g, 58%), b.p. 140–142 °C/0.18 mmHg (Found: C, 85.2; H, 8.2. $C_{16}H_{18}O$ requires C, 84.91; H, 8.02%); ν_{max}/cm^{-1} 1685 (CO, α,β-unsaturated); λ_{max}(EtOH)/nm 285 (log ε 4.31); δ_H 1.25–2.28 (m, $CH_2CH_2CH_2CH{=}CH_2$), 2.39–2.66 (m, 5-H), 2.63 (dt, J_{gem} 17, $J_{4,5trans}$ = $J_{4,2}$ = 2, 4-*trans*-H), 3.22 (ddd, J_{gem} 17, $J_{4,5cis}$ 9, and $J_{4,2}$ 2, 4-*cis*-H), 4.95 (d further split, $J_{5cis,CH=CH_2}$ 11, 5-CH=CH^aH^b), 4.98 (d further split, $J_{5trans,CH=CH_2}$ 17, CH=CHH^b), 5.78 (ddt, $J_{4,5\text{-}trans\text{-}pentenyl}$ 17, $J_{4,5\text{-}cis\text{-}pentenyl}$ 11, and $J_{4,3\text{-}pentenyl}$ 7, CH=CH_2), 6.53 (t, $J_{2,4}$ 2, 2-H) and 7.34–7.72 (m, ArH); δ_C 26.7 (t, pentene C-2), 31.3 (t, pentene C-1), 38.3 (t, pentene C-3), 35.6 (t, C-4), 46.3 (d, C-5), 114.8 (t, pentene C-5), 127.1 or 128.1 (d, C-2), 128.1 or 127.1, 129.0, 131.2 and 134.7 (ArC), 138.5 (d, pentene C-4), 172.1 (s, C-3) and 210.7 (s, C-1); *m*/*z* 226 (M^+, 6%), 171 (40), 158 (100), 128 (27) and 115 (25).

Photolysis Experiments

Photolysis of 5-(*but*-3-*enyl*)-3-*phenylcyclopent*-2-*enone* **3**.—(*a*) A solution of the cyclopentenone **3** (30 mg, 0.14 mmol) in nitrogen-degassed dry benzene (200 cm^3) was irradiated for 7 min. The solvent was removed under reduced pressure and the residue was shown by GC-MS to consist of the starting cyclopentenone **3** (97.7% recovery), *m*/*z* 212 (M^+, 2%), 158 (100), 128 (49) and 115 (54); and two photoproducts, compound **9** (1.5%), *m*/*z* (212, 20%), 144 (55), 129 (100), 128 (73), 115 (85), 77 (81) and 51 (68); and compound **10** (0.8%), *m*/*z* 212 (M^+, 14%), 158 (100), 128 (55) and 115 (67).

(*b*) A solution of the cyclopentenone **3** (10 mg, 0.04 mmol) in nitrogen-degassed dry benzene (150 cm^3) was irradiated for 15 min. Removal of the solvent under reduced pressure afforded an oil, which was shown to consist of the starting cyclopentenone **3** (77% recovery); and the photoproducts **9** (15%) and **10** (8%), identified by comparison of their mass spectra with those obtained above.

(*c*) A solution of the cyclopentenone **3** (55 mg, 0.26 mmol) in nitrogen-degassed dry benzene (250 cm^3) was irradiated for 36 min. Removal of the solvent under reduced pressure afforded an oil, which was shown by GC-MS to contain the starting cyclopentenone **3** and the photoproducts **9** and **10** in the proportions 9:60:31, identified by means of their mass spectra.

(*d*) A solution of the cyclopentenone **3** (10 mg, 0.04 mmol) in nitrogen-degassed dry benzene (150 cm^3) was irradiated for 12 h. Removal of the solvent under reduced pressure afforded an oil, which was shown by GC-MS to contain the photoproducts **9** and **10** in the ratio 95:5, identified by means of their mass spectra.

(*e*) A solution of the cyclopentenone **3** (2.80 g, 13.2 mmol), in portions of 60–70 mg in nitrogen-degassed dry benzene (250 cm^3), was irradiated for 40 min. The solvent was removed under reduced pressure and the crude products were combined and separated by flash chromatography into the starting material **3** (0.42 g, 15% recovery) and a mixture of 1-phenyltricyclo-[4.2.1.$0^{3,8}$]nonan-7-one **9** (1.38 g, 49%) and 8-phenyltricyclo[4.2.1.$0^{3,8}$]nonan-9-one **10**, which was distilled to give a yellow oil (1.02 g, 36%), b.p. 100–102 °C/0.5 mmHg, shown by GC-MS to consist of compounds **9** (72%) and **10** (28%); ν_{max}/cm^{-1} 1735 (CO); δ_H1.61–1.68 (2 H, m), 2.05–2.17 (2 H, m), 2.26–2.38 (2 H, m), 2.52–2.61 (2 H, m), 2.81–3.05 (3 H, m) and 7.08–7.35 (5 H, m, ArH).

The intensities of the signals in the ^{13}C NMR spectrum allowed the assignment of the peaks due to each product **9** and **10**, respectively. Isomer **9**: δ_C 23.9 (t), 34.0 (t), 36.3 (d, C-2), 36.6 (t), 43.5 (s, C-8), 46.7 (d, C-6), 48.3 (t), 52.3 (d, C-1), 125.0, 126.5, 129.0 and 149.7 (ArC) and 225.5 (s, C-7); isomer **10** δ_C 22.4 (t), 22.7 (t), 25.2 (t), 36.3 (t, C-2), 39.9 (d, C-3), 47.1 (d, C-1),* 48.9 (d, C-6),* 50.3 (s, C-8), 125.7, 126.9, 129.2 and 146.1 (ArC) and 224.3 (s, C-9).

(*f*) One series of irradiations produced a crude product, which was separated by flash chromatography into the starting material **3** and a mixture of the monomeric products **9** and **10** with a trace of the dimeric products (< 5%). The monomers and dimers were inseparable on TLC. Distillation of the product mixture yielded the monomers **9** and **10** with a trace of starting material **3** (< 5%), indicating that the dimers can revert to starting material when heated to temperatures of ~120 °C. The starting material **3** was subsequently removed by flash chromatography.

Photolysis of 1-*Phenyltricyclo*[4.2.1.$0^{3,8}$]*nonan*-7-*one* **9** *and* 8-*Phenyltricyclo*[4.2.1.$0^{3,8}$]*nonan*-9-*one* **10**.—A solution of the mixture **9** and **10** (97.3 mg, 0.46 mmol; ratio 2.4:1) in benzene (250 cm^3) was irradiated for 2.5 h. Removal of the solvent under reduced pressure afforded a yellow oil, which was diluted in diethyl ether (10 cm^3) and washed with saturated aq. sodium hydrogen carbonate (10 cm^3). The organic phase was dried ($MgSO_4$) and evaporated to afford a crude product (80.2 mg), shown by ^1H NMR and GC-MS to consist mainly of starting materials **9** (> 88%) and **10** (> 9%).

Photolysis of 5-(*Pent*-4-*enyl*)-3-*phenylcyclopent*-2-*enone* **4**.—A solution of the cyclopentenone **4** (2.60 mg, 11.5 mmol), in portions of 240–260 mg, in nitrogen-degassed dry benzene (250 cm^3), was irradiated for 1.5 h. The solvent was removed under reduced pressure to afford a yellow oil, which was purified by distillation to afford a solid (b.p. 100–120 °C/0.15 mmHg), which was recrystallised from ethyl acetate–hexane to give 9-*phenyltricyclo*[5.2.1.$0^{3,9}$]*decan*-10-*one* **11** (1.52 g, 58%), m.p. 110–111 °C (Found: C, 84.6; H, 8.0. $C_{16}H_{18}O$ requires C, 84.91: H, 8.02%); ν_{max}/cm^{-1} 1725 (CO); δ_H 1.74–1.31 (9 H, m),

* Signals may be interchanged.

Table 1 Products and yields (%)

Fraction	Yield (mg)	9	10	12	13	14	15
a	75	94	6				
b	127			98		2	
c	73			20		58	22
d	47			4	6		90
e	71			1	84		15

2.54 (dt, J_{gem} 12, $J_{6exo,7} = J_{6exo,5endo}$ 10, 6-*exo*-H), 2.78–2.84 (m, 1- and 6-H), 3.03 (ddt, $J_{7,6exo}$ 10, $J_{7,8syn}$ 3, and $J_{7,8anti} = J_{7,6endo}$ = 2, 7-H) and 7.23–7.37 (m, ArH); δ_C 21.4 (t, C-5 or -4), 22.8 (t, C-6), 28.5 (t, C-4 or -5), 33.4 (t, C-2), 42.2 (t, C-8), 43.8 (d, C-3), 50.2 (d, C-7), 50.7 (d, C-1), 53.3 (s, C-9), 125.4, 126.7, 129.3 and 148.7 (ArC) and 227.6 (s, C-10).

Baeyer–Villiger Oxidation of 1-*Phenyltricyclo*[4.2.1.0^{3,8}]-*nonan-7-one* **9** *and* 8-*Phenyltricyclo*[4.2.1.0^{3,8}]*nonan-9-one* **10**.—A mixture of the tricyclononanone **9** (117.4 mg, 0.55 mmol) and its isomer **10** (361.8 mg, 1.71 mmol), *m*-chloroperbenzoic acid (MCPBA) (0.71 g, 4.1 mmol) and lithium carbonate[16] (20 mg, 0.27 mmol) was stirred and heated under reflux in chloroform (20 cm^3) for 22 h. The reaction was quenched by the addition of saturated aq. sodium hydrogen carbonate (20 cm^3). The organic layer was separated and washed with aq. sodium hydrogen carbonate (3 × 20 cm^3). The combined aq. layers were extracted with chloroform (4 × 20 cm^3). The combined extracts were washed with water (20 cm^3) and dried ($MgSO_4$). Removal of the solvent under reduced pressure afforded a yellow oil (683 mg), which was separated by flash chromatography (17% ethyl acetate in hexane) into five fractions (a–e) containing six components (Table 1) as shown by GC-MS. Fraction (a) was identified by its ^{1}H and ^{13}C NMR spectra as a mixture of the starting tricyclononanones **9** and **10**.

Components **12–15** were separated by careful flash chromatography (17% ethyl acetate in hexane) of the combined fractions b–e, followed by recrystallisation from ethyl acetate–hexane to give four crystalline compounds (yields based on isolated yields from amount of ketone mixture) identified as:

(i) 1-*Phenyl*-8-*oxatricyclo*[4.3.1.0^{3,9}]*decan-7-one* **12** (83 mg, 19%), m.p. 110–111 °C (Found: C, 79.1; H, 7.1. $C_{15}H_{16}O_2$ requires C, 78.92; H, 7.06%); ν_{max}/cm^{-1} 1740; δ_H 1.64–2.31 (m, 10-H_2, 2-*exo*-H, 4- and 5-H_2), 2.36 (dd, J_{gem} 11.7, $J_{2endo,1}$ 8.8, 2-*endo*-H), 2.88–2.98 (m, 3-H), 3.01 (td, $J_{6,10}$ 7.1, $J_{6,5syn}$ 3.6, 6-H), 5.08 (d, $J_{3,9}$ 7.8, 9-H) and 7.18–7.38 (m, ArH); δ_C 22.6 (t, C-4 or -5), 24.7 (t, C-5 or -4), 30.3 (t, C-2), 35.3 (d, C-3), 41.0 (t, C-10), 41.2 (d, C-6), 47.9 (s, C-1), 80.4 (d, C-9), 125.3, 127.0, 129.4 and 149.3 (ArC) and 175.1 (s, C-7); *m*/*z* 228 (M$^+$, 23%), 171 (95), 129 (86), 115 (65), 91 (95) and 55 (100);

(ii) 8-*Phenyl*-4-*oxatricyclo*[4.2.2.0^{3,8}]*decan-5-one* **14** (43 mg, 8%), m.p. 114–115 °C (Found: C, 78.95; H, 7.1%); ν_{max}/cm^{-1} 1724; δ_H 1.72–1.82 (m, 10-H_2), 1.90 (dd, $J_{7exo,7endo}$ 13.9, $J_{7exo,6}$ 3.1, 7-*exo*-H), 1.99 (dd, $J_{2exo,1}$ 7.2, $J_{2exo,3}$ 3.9, 2-*exo*-H), 2.01–2.07 (m, 9-*anti*-H), 2.10 (ddd, J_{gem} 13.8, $J_{7endo,6}$ 3.0, $J_{7endo,10syn}$ 0.6, 7-*endo*-H), 2.29 (td further split, J_{gem} 12.5, $J_{9syn,10syn}$ 6.3, 9-*syn*-H), 2.77 (ddd, J_{gem} 14.4, $J_{2endo,1}$ 9.9, $J_{2endo,3}$ 8.5, 2-*endo*-H), 2.84–2.91 (m, 1-H), 3.09 (dtd, $J_{6,9anti}$ 12.2, $J_{6,7}$ 3.2, $J_{6,9syn}$ 1.7, 6-H), 5.05 (dt further split, $J_{3,2endo}$ 8.4, $J_{3,2exo}$ = $J_{3,1}$ = 2.4, 3-H) and 7.24–7.43 (m, ArH); δ_C 19.4 (t, C-9), 21.7 (t, C-10), 30.1 (t, C-7), 30.9 (t, C-2), 33.9 (d, C-6), 35.3 (d, C-1), 43.0 (s, C-8), 81.2 (d, C-3), 125.2, 126.6, 128.8 and 146.3 (ArC) and 176.3 (s, C-5); *m*/*z* 228 (M$^+$, 5%), 157 (28), 156 (100), 129 (26), 115 (25) and 91 (35);

(iii) 1-*Phenyl*-7-*oxatricyclo*[4.3.1.0^{3,9}]*decan*-8-*one* **13** (42 mg, 8%), m.p. 60.5–61.5 °C (Found: C, 79.0; H, 7.3%); ν_{max}/cm^{-1} 1740; δ_H 1.82–1.89 (m, 4-H_2), 1.98–2.22 (m, 10-H_2 and 5-*anti*-H), 2.23 (ddd, J_{gem} 11.7, $J_{2exo,3}$ 2, *J* 1, 2-*exo*-H), 2.44 (dt further split, J_{gem} 12–14, $J_{5syn,1}$ 6–8, 5-*syn*-H), 2.73 (ddd, J_{gem} 11.6, $J_{2endo,3}$ 9.5, $J_{2endo,10endo}$ 1.8, 2-*endo*-H), 2.83–2.94 (m, 3-H), 3.56 (d, $J_{3,9}$ 9.2, 9-H), 4.94 (ddd, $J_{6,5syn}$ 7.1, $J_{6,10exo}$ 4.4, $J_{6,10endo}$ 2.6, 6-H) and 7.08–7.40 (m, ArH); δ_C 23.5 (t, C-4), 26.8 (t, C-5), 29.5 (d, C-3), 33.5 (t, C-2), 42.6 (t, C-10), 44.0 (s, C-1), 47.8 (d, C-9), 76.3 (d, C-6), 124.3, 126.3, 128.8 and 148.9 (ArC) and 172.5 (s, C-8); *m*/*z* 228 (M$^+$, 11%), 200 (82), 173 (68), 115 (100), 83 (81) and 55 (91);

(iv) 8-*Phenyl*-5-*oxatricyclo*[4.2.2.0^{3,8}]*decan*-4-*one* **15** (45 mg, 9%), m.p. 80–81 °C (Found: C, 78.75; H, 7.0%); ν_{max}/cm^{-1} 1720–1730; δ_H 1.70–1.90 (m, 7-*endo*-H and 10-H_2), 1.98 (dd, J_{gem} 14.5, $J_{7exo,6}$ 2.2, 7-*exo*-H), 2.00 (ddd, J_{gem} 13.4, $J_{2exo,1}$ 8.1, $J_{2exo,3}$ 3.9, 2-*exo*-H), 2.13–2.27 (m, 9-*syn*-H), 2.32–2.45 (m, 9-*anti*-H), 2.78 (ddd, J_{gem} 13.4, $J_{2endo,3}$ 11.8, $J_{2endo,1}$ 10.2, 2-*endo*-H), 2.93–3.01 (m, 1-H), 3.50 (ddd, $J_{3,2endo}$ 11.8, $J_{3,2exo}$ 4.0, $J_{3,1}$ 1.1, 3-H), 4.95 (dddd, $J_{6,9anti}$ 9.2, $J_{6,7endo}$ 3.8, $J_{6,7exo}$ 2.3, $J_{6,9syn}$ 1.4, 6-H) and 7.23–7.43 (m, ArH); δ_C 21.6 (t, C-10), 24.2 (t, C-2), 25.6 (t, C-9), 33.4 (t, C-7), 36.6 (d, C-1), 40.1 (s, C-8), 42.6 (d, C-3), 74.3 (d, C-6), 125.0, 126.6, 128.8 and 147.1 (ArC) and 174.1 (s, C-4); *m*/*z* 228 (M$^+$, 3%), 200 (69), 117 (57), 115 (100), 91 (61) and 55 (55).

Baeyer–Villiger Oxidation of 9-*Phenyltricyclo*[5.2.1.0^{3,9}]-*decan*-10-*one* **11**.—MCPBA (280 mg, 1.30 mmol) and lithium carbonate (10 mg, 0.14 mmol) were added to a solution of the tricyclodecanone **11** (198 mg, 0.88 mmol) in chloroform (10 cm^3). The mixture was heated under reflux and stirred for 22 h. The reaction was quenched by the addition of saturated aq. sodium hydrogen carbonate (10 cm^3). The organic layer was separated, and washed with sodium hydrogen carbonate (3 × 10 cm^3), and the combined aqueous layers were extracted with chloroform (4 × 10 cm^3). The combined organic layers were dried ($MgSO_4$). Removal of the solvent under reduced pressure afforded a crude crystalline product (174 mg), which was shown (TLC) to consist of the starting material, and two products. The mixture was separated by flash chromatography into:

(i) 9-Phenyltricyclo[5.2.1.0^{3,9}]decan-10-one **11** (56.6 mg, 29% recovery);

(ii) 10-*Phenyl*-4-*oxatricyclo*[4.3.2.0^{3,10}]*undecan*-5-*one* **16** (56.1 mg, 28%), m.p. 162–163 °C (Found: C, 79.3; H, 7.7. $C_{16}H_{18}O_2$ requires C, 79.31; H, 7.49%); ν_{max}/cm^{-1} 1730; δ_H 1.54–1.66 (2 H, m, 9-*endo*-H and 7-, 8- or 11-H), 1.77–1.95 (3 H, m, 8-, 11-, and/or 7-H), 2.02–2.07 (2 H, m, 11-, 7- and/or 8-H), 2.11 (ddd, J_{gem} 15.0, $J_{2endo,1}$ 5.5, $J_{2endo,3}$ 2.6, 2-*endo*-H), 2.43 (br ddd, J_{gem} 13.4, $J_{9exo,8endo}$ 7.3, $J_{9exo,1}$ 3.7, 9-*exo*-H), 2.57 (ddd, J_{gem} 15.0, $J_{2exo,1}$ 10.7, $J_{2exo,3}$ 7.6, 2-exo-H), 3.02 (tt, $J_{6,7exo} = J_{6,11syn}$ = 4.9, $J_{6,7endo} = J_{6,11anti}$ = 3.6, 6-H), 3.12 (m, 1-H) 5.28 (ddd, $J_{3,2exo}$ 7.9, $J_{3,2endo}$ 2.5, $J_{3,1}$ 1.5, 3-H) and 7.21–7.75 (m, ArH); δ_C 21.9 (t, C-7, C-8 or C-11), 28.8 (t, C-2), 29.3 (t, C-8, C-11 or C-7), 35.4 (t, C-9), 37.9 (t, C-11, C-7 or C-8), 39.0 (d, C-6), 40.7 (d, C-1), 46.2 (s, C-10), 82.5 (d, C-3), 125.1, 126.4, 128.7 and 148.6 (ArC) and 174.0 (s, C-5);

(iii) 10-*Phenyl*-5-*oxatricyclo*[4.3.2.0^{3,10}]*undecan*-4-*one* **17** (48.5 mg, 24%), m.p. 100–101 °C (Found: 79.3; H, 7.6%); ν_{max}/cm^{-1} 1720; δ_H 1.53–1.70 (2 H, m, 9-*endo*-H and 7- or 8-H), 1.80–1.95 (3 H, m, 7-H and 8-H), 1.90 (ddd, J_{gem} 15.2, $J_{11syn,6}$ 7.3, $J_{11syn,7endo}$ 1.6, 11-*syn*-H), 2.01 (dd, J_{gem} 15.1, $J_{11anti,6}$ 0.6, 11-*anti*-H), 2.07 (dt, J_{gem} 13.4, $J_{2endo,1} = J_{2endo,3}$ = 3.7, 2-*endo*-H), 2.38–2.45 (m, 9-*exo*-H), 2.70 (ddd, J_{gem} 13.2, $J_{2exo,3}$ 11.7, $J_{2exo,1}$ 10.7, 2-*exo*-H), 3.06–3.10 (m, 1-H), 3.55 (ddd, $J_{3,2exo}$ 11.5, $J_{3,2endo}$ 3.5, $J_{3,1}$ 1.4, 3-H), 4.97 (t further split, $J_{6,7exo} = J_{6,11syn}$ = 5.1, 6-H) and 7.21–7.41 (m, ArH); δ_C 18.3 (t, C-7 or C-8), 24.1 (t, C-2), 29.7 (t, C-8 or C-7), 36.6 (t, C-9), 37.2 (t, C-11), 39.4 (d, C-3), 42.8 (d, C-1), 46.0 (s, C-10), 79.3 (d, C-6), 124.8, 126.4, 128.8 and 149.3 (ArC) and 174.9 (s, C-4).

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