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Photochemical [2 + 2] cycloaddition reactions of 6-alkenyl-3-phenylcyclohex-2-en-1-ones: using biradical conformation control to account for exceptions to the "rule of five"†‡

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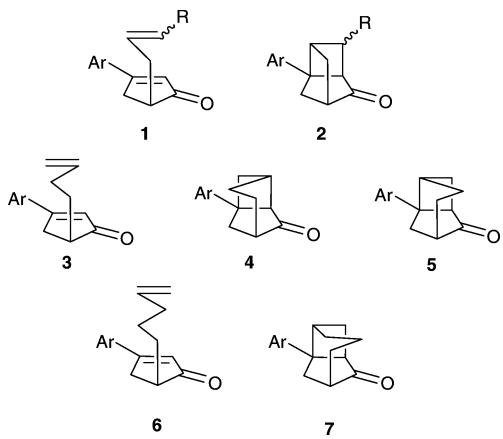
A series of 6-alkenyl-3-phenylcyclohex-2-enones has been synthesised and the structures of the products obtained from them on irradiation have been determined. The 6-propenyl compounds afforded a tricyclic 'parallel' [2 + 2] cycloaddition product and a bicyclic enone resulting from hydrogen abstraction in the biradical intermediate. The 6-butenyl and 6-pentenyl analogues gave 'crossed' cycloaddition products only. Although the regiochemistry of these cycloaddition reactions cannot be explained in terms of the 'rule of five', it is compatible with the concept of 'biradical conformation control' which is based on a consideration of the energy and structure of the possible 1,4-biradical intermediates.

Introduction

In previous work we have examined the photochemistry of 5-alkenyl-3-phenylcyclopentenones and have shown that **1** gave the so-called parallel[2] cycloaddition products **2**. This mode of addition was not changed by the presence of electron donating or withdrawing substituents in the *p*-position of the 3-phenyl group,[3] or by the presence of a phenyl group in the 2- or 3- positions of the propenyl side chain.[4,5] The last can also be substituted in the *p*-position by electron donating or withdrawing groups with no effect on the mode of cycloaddition.[6]

The related 5-(3′-butenyl)-3-phenylcyclopentenone **3** undergoes a similar photochemical reaction, but the major product **4** is the result of cross cycloaddition. The minor product **5** is formed through parallel cycloaddition. The homologue, 5-(4′-pentenyl)-3-phenylcyclopentenone **6**, gives a product **7**, which is formed by parallel cycloaddition[7] These results were rationalised using the "rule of five" initially proposed by Srinivasan[8] and Hammond,[9] and later explained by Gleiter[10] in terms of "through space" and "through bond" interactions.



Not all alkenyl substituted cycloalkenones are as well behaved in terms of the rule of five. The behaviour of 6-alkenylcyclohex-2-enones is of particular interest in this respect as they form the non-rule of five adduct, either exclusively or as the major product, on irradiation (Scheme 1). This behaviour is general for both simple 6-alkenylcyclohex-2-enones[11] and fused ring systems such as 1-alkenyl-2(1*H*)-naphthalenones.[12] This paper describes an extension of our previous work to 6-alkenyl-3-phenylcyclohex-2-enones; this work was carried out with a view to establishing whether or not the regiochemical outcome of the [2 + 2] cycloaddion reactions of these molecules would be consistent with the general behaviour of 6-alkenylcyclohex-2-enones, and to providing an explanation for the failure of such compounds to comply with the rule of five.

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‡ CCDC reference numbers 735146–735148. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c0ob01131b

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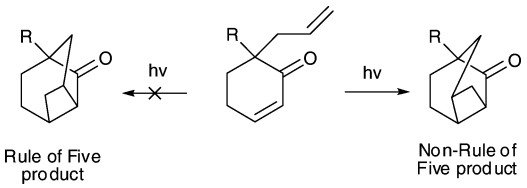


Scheme 1

Synthesis

Our original intention was to synthesise compounds of the type **8**, n = 1,2,3 (Scheme 2). We believed that the presence of the ester group would drive the equilibrium between the two possible conformations, **8′** and **8″**, towards **8′**, where the alkenyl side chain is "axial" and thus more favourably orientated for a [2 + 2] cycloaddition reaction. However the structure of **8**, n = 1, as determined by X-ray analysis (Fig. 1) shows that the molecule in the solid state adopts the conformation **8″**, in which it is the ester group which is "axial". Although in hindsight, this conformation may minimise repulsions between the carbonyl groups of the enone and ester, the finding does not affect our reasoning about the ratio of the two conformations in solution. While we were able to make the diketo-esters **9**, R = Me, Et from the appropriate alkyl 3-oxobutanoate and phenyl vinyl ketone, ring closure using a variety of bases and acids as catalysts resulted in concomitant loss of the ester group giving 3-phenylcyclohexenone **10** (Scheme 2).

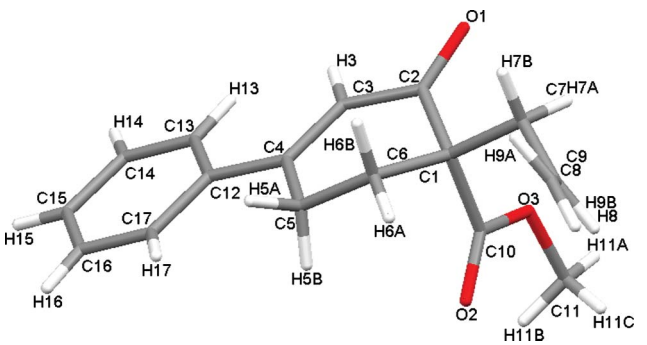
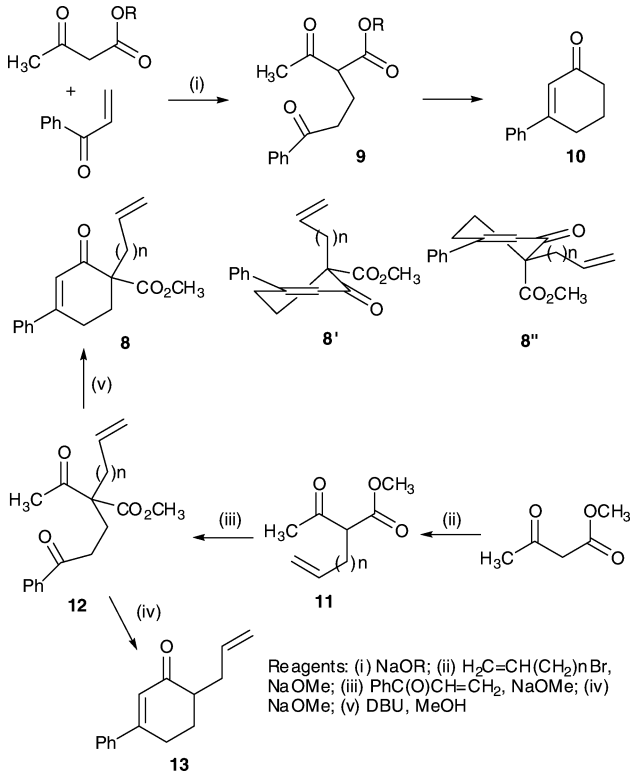
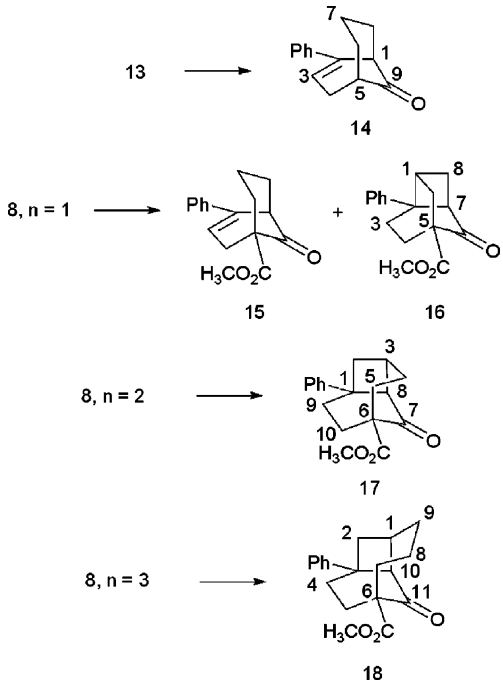


Fig. 1 3-Phenyl-6-(2′-propenyl)cyclohex-2-en-1-one, **8**, n = 1 (CCDC No. 735148).

In an alternative approach, we first attached the alkenyl groups to methyl 3-oxobutanoate to give **11**, n = 1,2,3, and then condensed these with phenyl vinyl ketone to afford **12**, n = 1,2,3. In a preliminary experiment with sodium methoxide, **12**, n = 1, was shown to undergo ring closure but again with loss of the ester group to afford **13**. However, using DBU as base, the compounds **12**, n = 1,2,3, all give the corresponding 6-alkenyl-6-methoxycarbonyl-3-phenyl-2-cyclohexenone **8**, n = 1,2,3. All the compounds were characterised by their ^{1}H- and ^{13}C-NMR spectra, using DEPT, nOe, and 2-D techniques.



Scheme 2



Scheme 3

Results

In the event, the presence of the ester group at the 6-position was not required, as when we irradiated the enone **13** in acetonitrile, a single product was obtained in 11% yield (Scheme 3). The reaction was followed by GCMS, as were the other photochemical reactions, and this confirmed the spectroscopic (NMR) finding that in all cases the isolated product(s) was the only low MW product(s) formed, and that no starting material remained unreacted. The presence of a styrene chromophore in these 3-phenylcyclopentenone systems results in polymerization being competitive with cycloaddition as a reaction channel, and accounts for the low yields observed. Polymer formation has also been observed in earlier work.[2] The ^{1}H-NMR spectrum

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showed that the allyl and enone olefinic hydrogens were no longer present, but that there was a triplet at δ 6.31. The product must therefore contain a new olefinic hydrogen coupled to a methylene group. The presence of a double bond was confirmed by the ^{13}C-NMR spectrum which contained signals at δ 125.7(CH) and 125.6(q). This suggests that after initial bond formation between the terminal carbon of the allylic group and the 2-position of the enone, hydrogen abstraction from the original 4-position of the enone, forming **14** with its styrene chromophore, occurs in preferenc to ring closure. ^{1}H- and ^{13}C-NMR data support this structure.

Photoreaction of the methyl ester **8**, n = 1, was complete after 12 h, and gave the corresponding keto-olefin **15** as the main product; this was never obtained in a pure state as it was always contaminated with a small amount of a minor component which was isolated from the mixture by low temperature crystallisation at −50 °C from hexane-ether (9 : 1). There was no olefinic signal in its ^{1}H-NMR spectrum. This spectrum and the ^{13}C-NMR spectrum, together with 2-D and nOe techniques, enabled us to identify this compound as **16**, the product of a parallel cycloaddition. Spectroscopically, the major component **15** showed the presence of a styrene residue and saturated carbonyl group. Irradiation of the higher homologue **8**, n = 2 (Scheme 3) was stopped after 14 h, and gave a single product **17** whose structure was confirmed by single crystal X-Ray analysis (Fig. 2). The NMR spectra were consistent with this structure. Decoupling, nOe, and 2-D techniques were used to identify the individual signals.

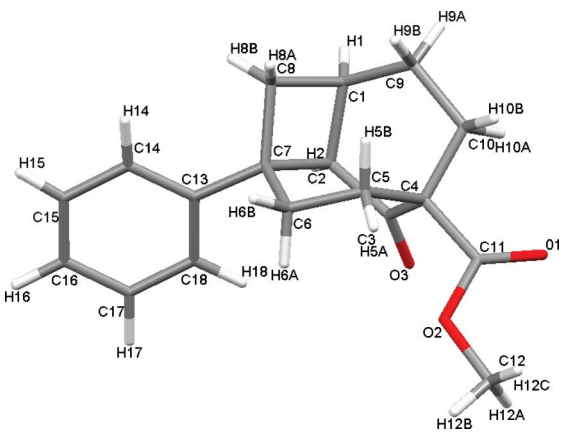


Fig. 2 Methyl 7-oxo-1-phenyltricyclo[4.2.2.0^{3,8}]decane-6-carboxylate **17** (CCDC No. 735146).

Similarly, the keto-ester **8**, n = 3, on irradiation (17 h) gave a single compound which was identified as the cross-product **18**. The structure was again determined by single crystal X-Ray analysis (Fig. 3); the NMR spectra obtained for the photoadduct were consistent with this structure.

Discussion

The "rule of five"[8,9,10] states that intramolecular [2 + 2] cycloaddition reactions will, where possible, occur *via* a 1,5-ring closure and the five-membered ring biradical thus formed. Although the rule provides a basis for rationalising the outcome of many [2 + 2] cycloaddition reactions, its application in some cases is less than convincing. The photochemical ring closure of 5-

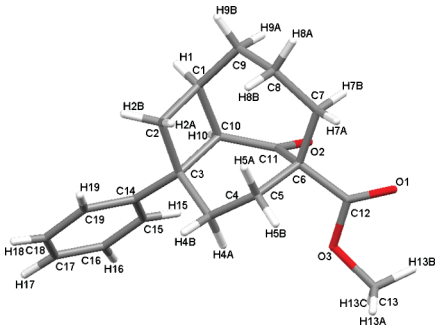
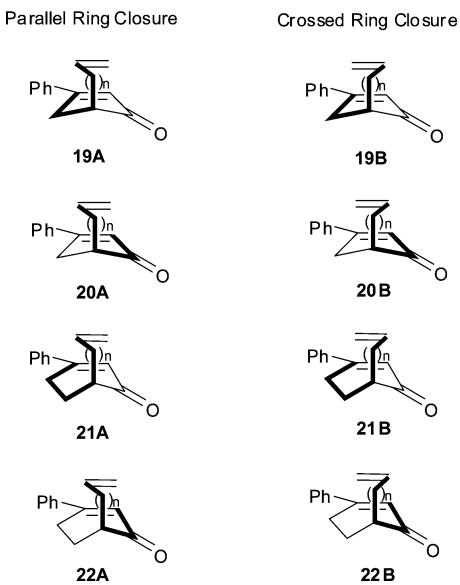


Fig. 3 Methyl 11-oxo-3-phenyltricyclo[4.3.2.0^{3,10}]undecane-6-carboxylate **18** [CCDC No. 735147].

allylcyclopentenones **1**[7] can, for example, be considered to proceed *via* a a 1,5-ring closure of alkene units which are in a 'parallel' orientation (**19A**; n = 1) (Scheme 4), resulting in the formation of **2**. Ring closure of alkene units in the corresponding 'crossed' orientation (**19B**; n = 1) would involve a 1,6 ring closure and is thus disfavoured by the rule of five. The successful application of the rule of five is however dependent on arbitrarily considering the alkene units to be connected by a pathway (**19A**, **19B**) which does not include the carbonyl group; considering this pathway results in an incorrect prediction of the regiochemical outcome of the reaction (**20A** and **20B**). Although a 1,5-closure is not possible for the 5-butenyl compound **3**, the regioselectivity observed in the formation of the major cycloadduct **4** can be accommodated by the extension to the rule of five which states that where 1,5-closure is not possible, the reaction should proceed by 1,6-closure. Unsatisfactorily however, such an approach only results in a correct regiochemical prediction if the pathway involving the carbonyl group, deliberately excluded above, is considered (**20B**; n = 2). The frontier orbital (FO) formulation of the rule of five due to Gleiter[10] suggests that alkenes connected by a bridge containing an odd number of carbon atoms should involve preferential parallel cycloaddition; if the connecting bridge contains an even



Scheme 4

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number of carbon atoms, cross addition should predominate. Assuming the pathway involving the carbonyl group is again arbitrarily excluded, the regiochemical outcome of the reactions of **1** and **3** is in keeping with this FO based version of the rule of five. It should be pointed out however that this approach is explicitly based[10] on the intermediacy of an exciplex, a species whose involvement in photochemical [2 + 2] cycloaddition reactions has been seriously questioned.[13] The basic rule of five has nothing to contribute in terms of rationalising the regioselectivity observed in the photoaddition of 5-(4′-pentenyl)-3-phenylcyclopenten-one **6**. If the pathway involving the carbonyl group is again ignored, the formation of **7** *via* a 1,7-ring closure (**19A**; $n = 3$) would be in keeping with Gleiter's FO analysis (odd, parallel).

Using the rule of five to rationalise the regiochemical outcome of the intramolecular [2 + 2] cycloaddition reactions of 6-alkenylcyclohexenones described in this paper is even less satisfactory. The formation of the parallel cycloadduct **16** on irradiation of **8**, $n = 1$, can be interpreted as a rule of five allowed, 1,6-closure (**21A**, $n = 1$), but only if one again arbitrarily ignores the 1,5-closure possible *via* the pathway containing the carbonyl group (**22B**, $n = 1$). It is worth noting that the regiochemical preference demonstrated by **8**, $n = 1$, in its cycloaddition reaction is shared by the structurally related, but electronically quite different, 1-methyl-1-allyl-2(1*H*)-naphthalenone.[12] Applying the FO approach is equally unsatisfactory as it suggests that irradiation of **8**, $n = 1$, should result in the formation of the incorrect regioisomer through the involvement of either **21B**, $n = 1$ (even, crossed) or **22B**, $n = 1$ (odd, parallel). The enone **8**, $n = 2$ has an extra carbon in the chain connecting the alkene units, but irradiation results in a reaction whose regiochemistry is inverted relative to that observed for **8**, $n = 1$. This means that the FO approach again fails to provide a rationalisation of the reaction outcome. The addition of a further methylene to the linking chain does not change the regiochemistry of the cycloaddition with **8**, $n = 3$, forming **18**: a prediction based on the FO approach would thus, almost by default, be correct. The basic rule is successful in relation to the formation of **17** from **8**, $n = 2$, as using the pathway containing the carbonyl group, **22B**, it can be considered to involve a 1,6-ring closure. It does not however provide any basis for dealing with the formation of **18** from **8**, $n = 3$. As it is clear that the rule of five in its basic form, or as formulated in terms of FO interactions, fails to provide an understanding of the photoaddition reactions of 6-alkenylcyclohexenones, a different mechanistic framework is thus required.

An alternative concept, biradical conformation control, has been successfully used to account for both the regiochemistry and stereochemistry of photochemical cycloaddition and cyclization reactions which involve biradical intermediates. Thus the regioselectivity of Paterno–Büchi[14] and intramolecular [2 + 2] cycloaddition reactions[15] has been rationalised in terms of this concept. The stereoselectivity of cyclizations of the Norrish/Yang type[16] and of those involving 1,5-biradicals[17,18] has also been satisfactorily explained, as has the stereoselectivity of the intramolecular addition of C–H bonds to cyclic enones[19] and that of Paterno–Büchi cycloadditions.[20] Thus, although a [2 + 2] cycloaddition may be a relatively complicated reaction in terms of the range of possible product determining intermediates, this body of work, together with trapping[21] and other data,[13] strongly argues that the outcome of the reaction is determined by the structure and behaviour of an intermediate 1,4-biradical.

The idea that the product determining factor in these photochemical reactions might be the conformation of the biradical intermediates derives from the fact that these are almost invariably of the triplet type. This means that they are sufficiently long-lived to allow conformational relaxation to occur, and that intersystem crossing (ISC) is required before the final bond forming step can take place. The rate of ISC depends on the level of spin–orbit coupling (SOC) within the biradical and this in turn is strongly dependent on its geometry,[22,23] specifically the inter-radical distance (IRD) and the relative orientation of the singly occupied p-orbitals. In the work described here the orientational potential for SOC in a particular biradical was evaluated qualitatively in terms of the level of interaction apparent in its spin density plot. Once ISC has occurred and the biradical is in the singlet state, the formation of closed shell products is very rapid and the opportunity for further conformational change is thus extremely limited. In the case of cycloaddition reactions this final step could result in the formation of a four-membered ring through ring closure, or the regeneration of the starting material(s) through bond cleavage. It is in fact reasonable to suggest that those biradicals which have undergone relatively efficient ISC would favour cyclobutane formation as the geometric factors facilitating ISC (short IRD and favourable orbital overlap) would also favour ring closure rather than bond cleavage. Biradicals which do not enjoy these structural features will not be product forming and will simply revert to starting material. Thus predicting the outcome of a cycloaddition involves identifying the biradical(s) which possess these structural characteristics and hence the product(s) that should be formed. An analysis of the photochemical behaviour described above for 6-alkenyl-3-phenylcyclohex-2-enones, in terms of this concept is set out in detail below.

As mentioned above intramolecular [2 + 2] cycloaddition in systems such as **8**, $n = 1$, 2, 3, and **13** can result in the formation of regioisomeric products as the interacting alkene units can orientate themselves relative to each other in a parallel or crossed fashion. A molecular modelling study of the biradicals derived from **8**, $n = 1$, 2, 3, and **13** was carried out with a view to evaluating the potential of the biradical conformational control concept as a tool for understanding the regiochemistry of these photochemical reactions. The study considered all possible biradicals, including those involving 1° radicals, as trapping experiments[23] have indicated that these can be formed as intermediates in the course of these photochemical [2 + 2] cycloaddition reactions. The approach involved initially identifying the low energy conformation(s) of each of the four possible biradicals using a semi-empirical (AM1) conformational search procedure. A DFT calculation (UB3YLP/6-31G*) was then used to refine the structure and energy of each low energy conformation. Potential product forming biradicals were identified on the basis of IRDs, and whether the spin density plots indicated that the singly occupied p-orbitals were favourably orientated relative to each other. Biradicals of high relative energy were however excluded, even if their structures were appropriate, on the basis that their formation would not be competitive.

None of the 1,4-biradicals that can be formed from **13** has a low energy conformation which would facilitate closure to a cyclobutane. The IRD in each case is greater than 3.00 Å (Table 1) and there is no overlap in any of the spin density plots at the 0.004 electrons/au^3 level, a value chosen empirically to facilitate a comparison of the spatial relationship of the singly occupied

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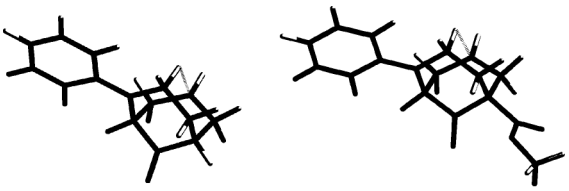
Table 1 Relative energies and inter-radical distances for biradicals

	1°/3° Crossed		2°/2° Crossed		1°/2° Parallel		2°/3° Parallel	
Enone	ΔE^a	IRD[b]	ΔE^a	IRD[b]	ΔE^a	IRD[b]	ΔE^a	IRD[b]
13	9.17	3.02	10.00	3.20	14.10	3.11	0.00	3.12
8, $n = 1$	7.90	3.02	10.16	3.18	13.40	3.02	0.00	3.13
8, $n = 2$	3.03	3.03	9.33	2.89	13.73	2.95	0.00	3.16
8, $n = 3$	4.97	2.90	11.78	2.79	16.75	2.87	0.00	3.17

[a] Energy relative to 2°/3° parallel biradical, kcal mol^{-1}; [b] inter-radical distance, Å.

p-orbitals in the various biradicals. Thus the expectation for this system is that cyclobutane formation would not occur, the biradicals instead undergoing bond cleavage to regenerate starting material. However the conformation of the lowest energy biradical (Table 1), the 2°/3° parallel biradical (Table 2, **A**), is set up for intramolecular hydrogen abstraction as it involves a very short carbon radical/hydrogen distance (2.67 Å), with the same atoms forming part of a six-membered chair arrangement (Fig. 4a). The fact that the hydrogen abstraction product **14** is actually formed on irradiation validates the biradical conformational control approach as a means of understanding the photochemical behaviour of these systems.



(a) C-radical/hydrogen distance in biradical derived from **13**: 2.67 Å

(b) C-radical/hydrogen distance in biradical derived from: **8, n = 1:** 2.62 Å

Fig. 4 Hydrogen abstraction forming **14** and **15**.

The molecular modelling analysis indicates that the biradical intermediates derived from the carbomethoxy substituted cyclohexenone **8**, $n = 1$, have lowest energy conformations that are almost identical to those of the biradicals derived from **13** (Table 1). Thus it is not surprising that the formation of the hydrogen abstraction product **15** should be observed, again produced *via* the biradical of lowest energy, the 2°/3° parallel biradical (Table 2, **B**; Fig. 4b). However in this case molecular modelling analysis of the 1°/2° parallel biradical obtained from **8**, $n = 1$, indicates that it has two low energy conformations of almost equal energy (ΔE = 0.12 kcal mol^{-1}). In contrast to the situation for **13**, there is a small degree of overlap in the spin density plot of the higher energy of these two biradicals at the 0.004 electrons/au^3 level (Table 2, **C**), thus accounting for the competitive formation of the parallel cycloadduct **16** on irradiation of this enone. Irradiation of the cyclohexenone **8**, $n = 2$, results in the regioselective formation of the crossed cycloadduct **17**. Molecular modelling indicates that overlap occurs in the spin density plots of the minimum energy forms of the 1°/2° parallel and the 2°/2° crossed biradicals. However the energy difference between the two (ΔE = 4.40 kcal mol^{-1}) (Table 1) suggests that the reaction should involve the latter (Table 2, **D**) and result in the formation of **17**. Although the corresponding parallel 2°/3° biradical (Table 2, **E**) is lowest in energy (Table 1), its singly occupied orbitals, as indicated in the spin density plot, are not appropriately orientated for ring closure and so it is not product forming. The observed formation of **17** is thus entirely in keeping with the principle of biradical conformation control.

The cyclohexenone **8**, $n = 3$, also forms a crossed cycloadduct, **18**, regioselectively. A consideration of the spin-density plots of the four possible biradical intermediates again indicates that the 2°/2° crossed (Table 2, **F**) and the 1°/2° parallel biradicals are potentially product forming, but that the observed product should be that derived from the former because of the significant energy difference (ΔE = 4.95 kcal mol^{-1}) between the two biradicals (Table 1). In this case there is the additional factor that the level of overlap in the spin density plot is also much greater for the crossed 2°/2° radical for which overlap occurs up to the 0.0063 electrons/au^3 level; overlap disappears at the 0.0045 electrons/au^3 level for the corresponding parallel 1°/2° biradical. The parallel 2°/3° biradical (Table 2, **G**), despite being lowest in energy, can again be excluded from the analysis as its singly occupied orbitals are not appropriately orientated for ring closure and therefore this biradical would be expected to undergo bond cleavage, reverting to starting material.

In view of the many exceptions,[24–27] to which the results presented here can be added, it is clear that the empirical 'rule of five' and the theoretical models which have been developed to support it, do not provide a basis for a comprehensive understanding of the outcome of intramolecular [2 + 2] cycloaddition reactions. The failure to allow for the effect of substituents is one obvious limitation. In contrast, the 'biradical conformation control' concept provides an understanding of the photochemical behaviour of these systems in terms of the energy and structure of what are the well-established intermediates in their reactions, with substituents playing a role in determining the structure of the minimum energy conformation of the intermediate. The results presented here suggest that the behaviour of other systems undergoing intramolecular photochemical [2 + 2] cycloaddition should be re-examined using this approach and this work is currently underway.

Experimental

Melting points are uncorrected. Solvents were dried and distilled. Photochemical experiments were carried out using an Applied Photophysics 400 W medium pressure mercury lamp and a Pyrex filter. These reactions were monitored by GC-MS. IR spectra were measured in cm^{-1} using Perkin Elmer Paragon 1000 or 1600 FT-IR machines as neat liquids, or as Nujol mulls. NMR spectra were recorded using a Varian Gemini 2000, Bruker MSL 300, or a Bruker DPX machine, using deuteriochloroform as solvent (unless otherwise stated). Peak positions are given in ppm from TMS, and J values in Hz. In the assignment of NMR signals, atoms in side-chains are indicated with an apostrophe (e.g. 2′). Calculations were performed using Spartan '04 (Wavefunction, Inc., Irvine, CA, 2004). An AM1 based conformational search procedure, based on the default Monte Carlo facility, was used to identify the low energy conformations for each biradical. The geometry of conformations with an inter-radical distance of less

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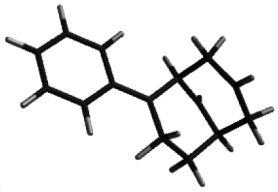
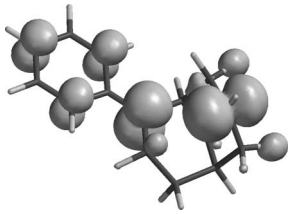
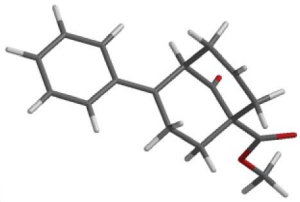
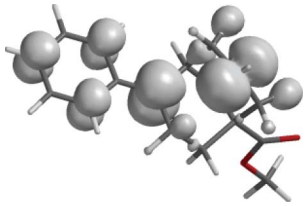
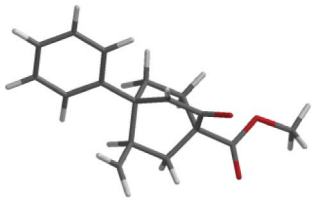
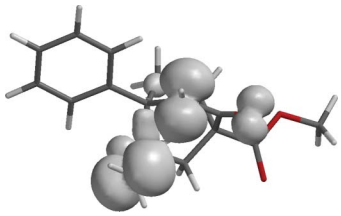
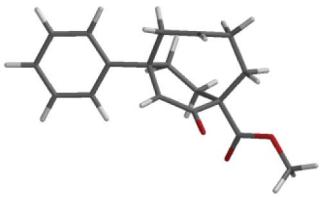
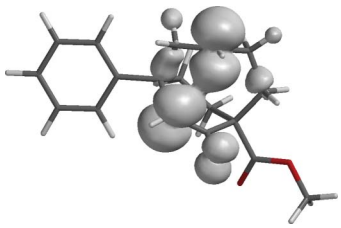
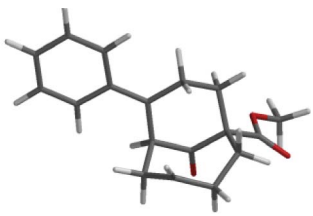
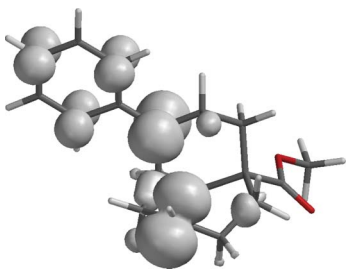
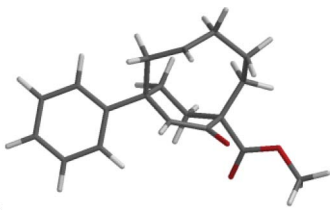
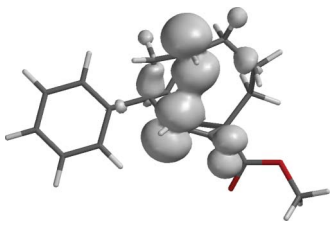
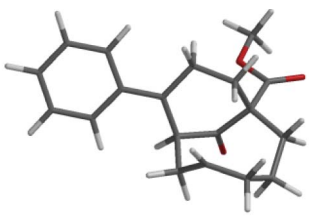
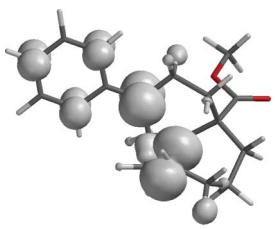
Table 2 UB3YLP/6-31G* derived biradical structures

Enone	Biradical	Minimum Energy Conformer	Spin Density Surface
13	Parallel, 2°/3°	**A** 	
8, $n = 1$	Parallel, 2°/3°	**B** 	
8, $n = 1$	Parallel, 1°/2°	**C** 	
8, $n = 2$	Crossed, 2°/2°	**D** 	
8, $n = 2$	Parallel, 2°/3°	**E** 	
8, $n = 3$	Crossed, 2°/2°	**F** 	
8, $n = 3$	Parallel, 2°/3°	**G** 	

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than 3.5 Å were then refined using a DFT (UB3LYP/6-31G*) optimization.

Crystal data

3-Phenyl-6-(2′-propenyl)cyclohex-2-en-1-one 13 (Fig. 1). $C_{17}H_{18}O_3$, M = 270.31, Triclinic, a = 6.121(6), b = 10.219(3), c = 12.1028(18) Å, α = 80.995(17), β = 83.01(3), γ = 82.18(5), U = 736.9(8) Å^3, T = 298 K, space group $P\bar{1}$, Z = 2, μ(Mo-Kα) = 0.08 mm^{-1}, 2843 reflections collected, 1387 unique, (R_{int} = 0.0176), [a] R_1 = 0.0527, $wR2$ [$I > 2\sigma(I)$] = 0.1294, Gof = 1.033, CCDC deposition number 735148.

Methyl 7-oxo-1-phenyltricyclo[4.2.2.0^{3,8}]decane-6-carboxylate 17 (Fig.2). $C_{18}H_{20}O_3$, M = 284.34, Triclinic, a = 6.6572(9), b = 9.8399(8), c = 12.3209(15) Å, α = 102.795(8), β = 99.112(11), γ = 105.356(9), U = 738.47(15) Å^3, T = 298 K, space group $P\bar{1}$, Z = 2, μ(Mo-Kα) = 0.09 mm^{-1}, 2763 reflections collected, 1396 unique, (R_{int} 0.0325), [a] R_1 = 0.0507, $wR2$ [$I > 2\sigma(I)$] = 0.1283, Gof = 1.001, CCDC deposition number 735146.

Methyl 11-oxo-3-phenyltricyclo[4.3.2.0^{3,10}]undecane-6-carboxylate 18 (Fig.3). $C_{19}H_{22}O_3$, M = 298.37, Triclinic, a = 6.6266(7), b = 10.1023(10), c = 12.3043(11) Å, α = 90.769(8), β = 96.613(10), γ = 103.782(8), U = 793.91(14) Å^3, T = 298 K, space group $P\bar{1}$, Z = 2, μ(Mo-Kα) = 0.08 mm^{-1}, 2133 reflections collected, 1578 unique, (R_{int} 0.0183), [a] R_1 = 0.0373, $wR2$ [$I > 2\sigma(I)$] = 0.1003, Gof = 1.086, CCDC deposition number 735147.

$$^{a}R_1 = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |,$$

$$wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$$

Synthesis

Methyl 2-acetyl-5-oxo-5-phenyl-2-(2′propenyl)pentanoate 12, *n* = 1. Sodium methoxide [from sodium (0.2 g, 12 mmol)] in methanol (10 mL) was added slowly to a stirred mixture of methyl 2-acetylpent-4-enoate (4.00 g, 25.6 mmol) and phenyl vinyl ketone (3.38 g, 25.6 mmol) at 0 °C. The mixture was stirred at this temperature for 1 h, then acidified using aqueous hydrochloric acid (20 mL, 1 M), and extracted with dichloromethane (3 × 30 mL). The combined organic layers were washed with water, and dried ($MgSO_4$). The solvent was removed *in vacuo* and the residue was fractionally distilled to give **12**, n = 1 as a viscous oil (3.91 g, 53%); bp 162–164 °C/0.3 mbar; IR ν_{max} (neat) 1741, 1712, and 1686 cm^{-1}; ^{1}H NMR δ (200 MHz) 2.11 (3H, s, acetyl CH_3), 2.22–2.29 (2H, m, 3-H), 2.61 (2H, br d, 1′-CH_2), 2.84 (2H, m, 4-H), 3.66 (3H, s, ester CH_3), 5.04 (2H, m, 3′-CH_2), 5.60 (1H, ddt, J = 17.2, 9.9, and 7.3, 2′-CH), 7.34- 7.48 (3H, m, *m*- and *p*-PhH), 7.86 (2H, m, *o*-PhH); ^{13}C NMR δ (50 MHz) 25.7 (3-C), 26.6 (acetyl CH_3), 32.9 (4-C), 36.7 (1′-C), 52.1 (ester CH_3), 62.3 (2-C), 119.0 (2′-C), 127.8 (2′-C and *o*-PhC), 128.4 (*m*-PhC), 131.9 (*p*-PhC), 136.4 (*ipso*-PhC), 172.0 (1-C), 198.6 (5-C), and 202.4 (acetyl C═O). Found: C, 70.68; H, 7.15. $C_{17}H_{20}O_4$ requires C, 70.81; H, 6.99%.

Ethyl 2-acetyl-5-oxo-5-phenyl-2-(2′-propenyl)pentanoate. Sodium ethoxide [from sodium (0.05 g, 2 mmol)] in ethanol (10 mL) was added slowly to a stirred mixture of ethyl 2-acetylpent-4-enoate (12.87 g, 75.7 mmol) and phenyl vinyl ketone (10.00 g, 75.7 mmol) at 0 °C, and the reaction maintained at this temperature for 1h. The mixture was acidified with aqueous hydrochloric acid (20 mL, 1 M) and extracted with dichloromethane (3 × 30 mL). The combined organic layers were washed with water, and dried ($MgSO_4$). The solvent was removed and the residue distilled to give an oil (13.57 g, bp 172–176 °C/0.7 mbar). The oil was dissolved in hexane/ether (9 : 1) at –40 °C to give a precipitate, which was washed with hexane/ether (9 : 1) at –40 °C. The product was dried in a desiccator *in vacuo* to give ethyl 2-acetyl-5-oxo-5-phenyl-2-(2′-propenyl)pentanoate (10.99 g, 53%), mp 48–49 °C. IR ν_{max} (nujol) 1737, 1712, and 1686 cm^{-1}; ^{1}H NMR δ (200 MHz) 1.25 (3H, t, J = 7.2, ester CH_3), 2.17 (3H, s, acetyl CH_3), 2.28 (2H, m, 3-H), 2.65 (2H, d, J = 7.2, 1′-CH_2), 2.88 (2H, m, 4-H), 4.2 (2H, q, J = 7.2, ester CH_2), 5.10 (2H, m, 3′-CH_2), 5.62 (1H, ddt, J = 17.0, 10.5, and 6.7, 5-H, 2′-CH), 7.49 (3H, m, *m*- and *p*-PhH), and 7.92 (2H, m, *o*-PhH); ^{13}C NMR δ 13.9 (ester CH_3) 25.9 (3-C), 26.8 (acetyl CH_3), 33.1 (4-C), 36.8 (1′-C), 61.4 (ester CH_2), 62.5 (2-C), 119.2 (3′-C), 128.0 (*o*-PhC), 128.6 (*m*-PhC), 132.0 (*p*-PhC), 133.1 (2′-C), 136.6 (*ipso*-PhC), 171.7 (1-C), 198.8 (5-C), and 204.7 (acetyl C═O). Found: C, 71.41; H, 7.29. $C_{18}H_{22}O_4$ requires C, 71.50; H, 7.33%.

Methyl 2-oxo-4-phenyl-1-(2′-propenyl)cyclohex-3-ene-1-carboxylate 8, *n* = 1. A mixture of the diketo methyl ester **12**, n = 1 (6.29 g, 21.8 mmol) and DBU (3.32 g, 21.8 mmol) in methanol (50 mL) were refluxed for 30 min. The mixture was acidified with aqueous hydrochloric acid (30 mL, 1 M), and extracted with dichloromethane (3 × 50 mL). The combined organic layers were washed with dilute hydrochloric acid (50 mL) and water (50 mL), and then dried ($MgSO_4$). Removal of the solvent, and distillation of the residue gave an oil (4.02 g, bp 162–165 °C/2 mbar). The oil was dissolved in hexane/ether (8 : 2, 20 mL) and cooled to –50 °C to give a white precipitate. The product was washed with hexane/ether (8 : 2) at –50 °C, and dried in a desiccator *in vacuo* to give the keto ester **8**, n = 1, as needles, mp 65–66 °C, (2.95 g, 47%); IR ν_{max} (Nujol) 1728, 1671, and 1640 cm^{-1}; ^{1}H NMR δ (400 MHz) 2.10 (1H, ddd, J = 14.0, 9.5, 5.0, 6_{ax}-H), 2.60 (2H, m, 6_{eq}-H and 1a′-CH_2), 2.77 (2H, m, 5_{ax}-H and 1b′-CH_2), 2.94 (1H, dddd, J = 18.5, 9.3, 5.0, and 2.0, 5_{eq}-H), 3.72 (3H, s, ester CH_3), 5.15 (2H, m, 3′-CH_2), 5.80 (1H, ddt, J = 17.5, 10.0, and 7.2, 2′-H), 6.47 (1H, br s, 3-H), 7.41 (3H, m, *m*- and *p*-PhH) and 7.55 (2H, m, *o*-PhH); ^{13}C NMR δ (80 MHz) 25.3 (5-C), 29.8 (6-C), 38.4 (1′-C), 52.3 (ester CH_3), 55.3 (1-C), 118.8 (3′-C), 124.2 (3-C), 126.2 (*o*-PhC), 128.7 (*m*-PhC), 130.2 (*p*-PhC), 133.2 (2′-C), 137.9 (*ipso*-PhC), 158.5 (4-C), 171.5 (ester C) and 195.0 (2-C). Found: C, 75.58; H, 6.56%. $C_{17}H_{18}O_3$ requires C, 75.53; H, 6.71.

3-Phenyl-6-(2′-propenyl)cyclohex-2-en-1-one 13. Sodium hydride (850 mg, 35.4 mmol) and ethyl 2-acetyl-5-oxo- 5-phenyl-2-(2′-propenyl)-pentanoate (10.0 g, 33.1 mmol) in tetrahydrofuran (50 mL) were refluxed for 1 h. The mixture was acidified with aqueous hydrochloric acid (50 mL, 1 M) and extracted with dichloromethane (3 × 50 mL). The combined organic layers were washed with hydrochloric acid and water, and then dried ($MgSO_4$). Removal of the solvent and distillation of the residue afforded an oil, bp 165–170 °C. This oil was dissolved in acetone (30 mL) and cooled to –75 °C, to afford a colourless precipitate which was collected, and washed with acetone (10 mL) at –75 °C. The product was dried in a desiccator *in vacuo*, to give the cyclohexenone **13** (4.96 g, 70%) mp 49 °C; IR ν_{max} (neat) 1669, 1651, and 1649 cm^{-1}; ^{1}H NMR δ (400 MHz) 1.89 (1H, dddd, J = 13.6, 11.5, 9.5, and

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5.5, 5_{ax}-H), 2.18–2.30 (2H, m, 5_{eq}- and 1b′-CH_2), 2.42 (1H, ddt, J = 11.5, 8.8, and 4.5, 6-H), 2.73 (2H, m, 4_{ax}-H and 1a′-CH_2), 2.83 (1H, m, 4_{eq}-H), 5.10 (2H, m, 3′-CH_2), 5.85 (1H, m, 2′-H), 6.43 (1H, partially resolved d, J = 1.5, 2-H), 7.42, (3H, m, *m*- and *p*-PhH), and 7.55 (2H, m, *o*-PhH); ^{13}C NMR δ (80 MHz) 27.4 (5-C), 27.43 (4-C), 33.7 (1′-C), 45.3 (6-C), 116.7 (3′-C), 125.0 (2-C), 126.6 (*o*-PhC), 128.7 (*m*-PhC), 129.6 (*p*-PhC), 136.1 (2′-C), 138.6 (*ipso*-PhC), 158.6 (6-C) and 200.7 (1-C). Found: C, 84.73; H, 7.56. $C_{15}H_{16}O$ requires C, 84.87; H, 7.60%.

Methyl 2-acetylhex-5-enoate 11, *n* = 2. Methyl 3-oxobutanoate (8.59 g, 74.0 mmol) was added to a solution of sodium methoxide [from sodium (1.75 g, 74.0 mmol)] in methanol (100 mL). 4-Bromo-1-butene (10 g, 74.0 mmol) was added over 10 min, and the mixture refluxed for 7 h. The solvent was removed, and the residue acidified with dilute hydrochloric acid (30 mL, 1 M) and extracted with diethyl ether (3 × 100 mL). The combined ether layers were dried ($MgSO_4$), and the solvent removed. Fractional distillation of the residue gave the ketoester **11**, n = 2 as a colourless oil (6.92 g, 55%), bp 67–69 °C/0.5 mmbar; IR ν_{max} (neat) 1741, 1717, and 1641 cm^{-1}; ^{1}H NMR δ (400 MHz) 1.78 (2H, m, 3-H), 1.90 (2H, 4-H), 2.06 (acetyl CH_3), 3.33 (1H, t, J = 7, 2-H), 3.57 (3H, s, ester CH_3), 4.86 (2H, m, 6-CH_2), 5.70 (1H, ddt, J = 16.7, 10.0, and 6.6, 5-H); ^{13}C NMR δ (80 MHz) 26.7 (3-C), 28.5 (acetyl CH_3), 30.4 (4-C), 51.8 (ester CH_3), 58.1 (2-C), 115.4 (6-C), 136.6 (5-C), 169.7 (1-C), and 202.3 (acetyl C═O). Found: C, 63.53; H, 8.2%. $C_9H_{14}O_3$ requires C, 63.51; H, 8.29.

Methyl 2-acetyl-2-(3-oxo-3-phenylpropyl)hex-5-enoate 12, *n* = 2. Sodium methoxide [from sodium (0.2 g, 12.0 mmol)] in methanol (10 mL) was added slowly to a stirred mixture of methyl 2-acetylhex-4-enoate **11**, n = 2 (12.8 g, 75.7 mmol) and phenyl vinyl ketone (10.0 g, 75.7 mmol) at 0 °C. The mixture was stirred at this temperature for 1 h, acidified with dilute hydrochloric acid (20 mL, 1 M), and extracted with dichloromethane (3 × 30 mL). The combined organic layers were dried ($MgSO_4$), and the solvent removed. The residue was fractionally distilled to give the diketoester **12**, n = 2 as a viscous oil (11.62 g, 51%), bp 170–172 °C/0.5 mmbar; IR ν_{max} (neat) 1741, 1712, and 1686 cm^{-1}; ^{1}H NMR δ (200 MHz) 1.92 (2H, m, 3-CH_2), 2.11 (3H, s, acetyl CH_3), 2.17 (2H, m, 4-CH_2), 2.28 (2H, m, 1′-CH_2), 2.82 (2H, m, 2′-CH_2), 3.67 (3H, s, ester CH_3), 5.06 (2H, m, 6-CH_2), 5.60 (1H, ddt, J = 17.0, 10.5, and 6.7, 5-H), 7.45 (3H, m, *m*- and *p*-PhH), and 7.87 (2H, m, *o*-H); ^{13}C NMR δ (50 MHz) 25.7 (1′-C), 26.7 (acetyl CH_3), 34.4 (3-C), 30.4 (4-C), 32.4 (2′-C), 52.2 (ester CH_3), 62.3 (2-C), 117.0 (6-C), 127.8 (*o*-PhC), 130.4 (5-C), 128.4 (*m*-PhC), 131.9 (*p*-PhC), 136.6 (*ipso*-PhC), 172.6 (1-C), 198.6 (3′-C), and 202.7 (acetyl C═O). Found: C, 71.38; H, 7.39%. $C_{18}H_{22}O_4$ requires C, 71.5; H, 7.33.

Methyl 2-oxo-4-phenyl-1-(3′-butenyl)cyclohex-3-ene-1-carboxylate 8, *n* = 2. Methyl 2-acetyl-(3-oxo-3-phenylpropyl)hex-5-enoate **12**, n = 2 (6.00 g, 19.8 mmol), DBU (3.01 g, 19.8 mmol) and methanol (10 mL) were refluxed for 30 min. The mixture was acidified with dilute hydrochloric acid (30 mL, 1 M), and then extracted with dichloromethane (3 × 50 mL). The combined organic layers were washed with dilute hydrochloric acid and water, and were dried ($MgSO_4$). Removal of the solvent and fractional distillation of the residue gave a yellow oil (3.75 g, bp 184–189 °C/0.6 mbar). The oil was dissolved in hexane/ether (8 : 2, 20 mL) and cooled to −50 °C to give a white precipitate, which was collected and washed at −50 °C with hexane/ether (8 : 2). The solid was dried in air and then in a desiccator *in vacuo*. The product (2.93 g, 52%) had mp 67–68 °C; IR ν_{max} (neat) 1723, 1665, and 1638 cm^{-1}; ^{1}H NMR δ (400 MHz) 2.10 (5H, m, 1′- and 2′-CH_2, and 6_{ax}-H), 2.51 (1H, m, 6_{eq}-H), 2.78 (1H, m, 5_{ax}-H), 2.95 (1H, m, 5_{eq}-H), 3.72 (3H, s, ester-CH_3), 5.07 (2H, m, 4′-H), 5.80 (1H, ddt, J = 17.1, 10.0, and 7.0, 5′-H), 6.45 (1H, br s, 3-H), 7.42 (3H, m, *m*- and *p*-PhH), and 7.55 (2H, m, *o*-PhH); ^{13}C NMR δ (80 MHz) 25.3 (5-C), 29.9 (6-C), 33.1 (1′-C), 36.4 (2′-C), 52.3 (ester CH_3), 55.7 (1-C), 115.1 (4′-C), 124.3 (3-C), 126.1 (*o*-PhC), 128.7 (*m*-PhC), 130.1 (*p*-PhC), 137.4 (3′-C), 138.0 (*ipso*-PhC), 158.2 (4-C), 171.0 (ester C═O), and 195.4 (2-C). Found: C, 76.08; H, 7.15.%. $C_{18}H_{20}O_3$ requires C, 76.03, H, 7.09.

Methyl 2-acetylhept-6-enoate 11, *n* = 3. Methyl 3-oxobutanoate (9.24 g, 70.0 mmol) was added to a solution of sodium methoxide [from sodium (1.66 g 72.0 mmol)] in methanol. 5-Bromo-1-pentene (10.0 g, 67.0 mmol) was added over 10 min, and the mixture refluxed for 8 h. The solvent was removed and the residue was acidified with hydrochloric acid (30 mL, 1 M) and extracted with dichloromethane (3 × 50 mL). The combined organic layers were washed with water and dried ($MgSO_4$). The solvent was removed *in vacuo* and the residue distilled to give the ketoester **11**, n = 3 as a colourless oil, bp 60–62 °C/3.0 mbar; IR ν_{max} (neat) 1744, 1717, and 1641 cm^{-1}; ^{1}H NMR δ (400 MHz) 1.36 (2H, m, 4-CH_2), 1.83 (2H, m, 3-CH_2), 2.05 (2H, q, J = 7-H, 5-CH_2), 2.20 (3H, s, acetyl CH_3), 3.41 (1H, t, J = 7.5, 2-H), 3.71 (ester CH_3), 4.96 (2H, m, 7-CH_2), 5.75 (1H, ddt, J = 17.0, 10.3, and 6.6, 6-H); ^{13}C NMR δ (80 MHz) 26.5 (4-C), 27.5 (3-C), 28.6 (acetyl CH_3), 33.2 (5-C), 52.2 (ester CH_3), 59.4 (2-C), 114.9 (7-C), 137.6 (6-C), 170.1 (1-C), and 202.8 (acetyl C═O). Found: C, 65.09; H, 8.66%. $C_{10}H_{16}O_3$ requires C, 65.23; H, 8.75.

Methyl 2-acetyl-2-(3-oxo-3-phenylpropyl)hept-6-enoate (12, *n* = 3). Sodium methoxide [from sodium (0.2 g, 12 mmol)] 1n methanol (10 mL) was added slowly to a stirred mixture of methyl 2-acetylhept-6-enoate (4.0 g, 25.6 mmol) and phenyl vinyl ketone (3.36 g, 25.6 mmol) at 0 °C. The resulting mixture was stirred at this temperature for 1 h, acidified with dilute hydrochloric acid (20 mL, 1 M), and extracted with dichloromethane (3 × 30 mL). The combined organic layers were washed with water and dried ($MgSO_4$). The solvent was removed *in vacuo* and the residue distilled to afford the diketoester **12**, n = 3 as a viscous yellow oil (3.91 g, 53%), bp 162–164 °C/0.3 mbar. IR ν_{max} (neat) 1741, 1712, and 1686 cm^{-1}; ^{1}H NMR δ (200 MHz) 1.21 (2H, m, 4-H), 1.84 (2H, m, 3-H), 2.04 (2H, m, 5-H), 2.11 (acetyl CH_3), 2.25 (2H, m, 1′-CH_2), 2.79 (2H, m, 2′-CH_2), 3.67 (ester CH_3), 4.94 (2H, m, 7-CH_2), 5.60 (1H, ddt, J = 16.5, 10.5, and 6.6, 6-CH), 7.38 (2H, m, *m*-PhH), 7.48 (1H, m, *o*-PhH), and 7.87 (2H, m, *p*-PhH); ^{13}C NMR δ (50 MHz) 23.0 (4-C), 25.7 (1′-C), 26.6 (acetyl CH_3), 31.6 (3-C), 33.1 (2-′C), 33.5 (5-C), 52.0 (ester CH_3), 62.4 (2-C), 115.0 (7-C), 127.7 (*o*-PhC), 128.3 (*m*-PhC), 132.8 (*p*-PhC), 136.4 (*ipso*-PhC), 172.4 (1-C), 198.5 (3′-C), and 202.7 (acetyl C═O). Found: C, 72.26; H, 7.15%. $C_{17}H_{20}O_4$ requires C, 72.13; H, 7.33.

Methyl 2-oxo-4-phenyl-1-(4′-pentenyl)cyclohex-3-ene-1-carboxylate 8, *n* = 3. Methyl 2-acetyl-2-(3-oxo-3-phenylpropyl)hept-6-enoate **12**, n = 3 (7.2 g, 22.7 mmol), DBU (3.46 g, 22.7 mmol) and methanol (50 mL) were refluxed for 30 min. The mixture was

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acidified with dilute hydrochloric acid (30 mL, 1 M), and extracted with dichloromethane (3 × 50 mL). The combined organic layers were washed with dilute hydrochloric acid (50 mL) and water, and then dried ($MgSO_4$). The solvent was removed *in vacuo*, and the residue distilled to give a yellow oil (3.75 g, bp 184–189 °C/0.6 mbar). The oil was dissolved in hexane/ether (8 : 2) and cooled to −50 °C to afford a white precipitate, which was collected and washed with the same solvent at −50 °C. The product was dried (desiccator) to give the cyclohexenone **8**, $n = 3$ (3.39 g, 50%), mp 70–72 °C; IR ν_{max} (Nujol) 1723, 1665, and 1638 cm^{-1}; ^1H NMR δ 1.45 (2H, m, 2′-H), 1.82 (1H, m, 1′-H), 2.06 (4H, m, 6_{ax}-H, 3′-CH_2, 1′-H), 2.64 (1H, dt, $J = 13.5$, and 5.0, 6_{eq}-H), 2.76 (1H, dt, $J = 18.5$, and 5.0, 5_{ax}-H), 2.95 (1H, m, 5_{eq}-H), 3.72 (3H, s, ester CH_3), 5.01 (2H, m, 5′-CH_2), 5.81 (1H, ddt, $J = 17.0$, 10.0, and 6.7, 4′-H), 6.46 (1H, br s, 3-H), 7.42 (3H, *m*- and *p*-PhH), and 7.56 (2H, m, *o*-PhH); ^{13}C NMR δ 23.9 (2′-C), 25.4 (5-C), 29.9 (6-C), 33.3 (1′-C), 33,9 (3′-C), 52.3 (ester CH_3), 56.1 (1-C), 114.8 (5′-C), 124.3 (3-C), 126.0 (*o*-PhC), 128.7 (*m*-PhC), 130.1 (*p*-PhC), 138.0 (4′-C), 138.1 (*ipso*-PhC), 158.1 (4-C), 172.0 (ester C═O), and 196.1 (2-C). Found: C, 76.38; H, 7.50%. $C_{19}H_{22}O_3$ requires C, 76.48; H, 7.43.

Photochemical reactions

2-Phenyl-bicyclo[3.3.1]non-2-en-9-one 14. 3-Phenyl-6-(2′-propenyl)cyclohex-2-en-1-one **13** (1.74 g) in acetonitrile (450 mL) was irradiated for 2 h. The solvent was removed *in vacuo* to give a viscous oil, which was purified by flash chromatography (hexane/ether, 9 : 1) and trituration with the same solvent mixture to give white needles. The filtrate was cooled to −50 °C, when more precipitate formed. The solids were combined to afford the bicyclic ketone **14**[28] (total yield, 185 mg, 11%), mp 40–41 °C; ^1H NMR δ (400 MHz) 1.57 (1H, br s, 7_{exo}-H), 1.95 (5H, m, 6_{exo}-H, 6_{endo}-H, 7_{endo}-H, 8_{exo}-H, and 8_{endo}-H), 2.60 (1H, dd, $J = 19.0$ and 4.0, 4_{exo}-H), 2.62 (1H, m, 5-H), 2.89 (1H, m, 4_{endo}-H), 3.41 (1H, s, 1-H), 6.31 (1H, t, $J = 3.5$, 3-H), 7.30 (1H, m, *p*-PhH), and 7.40 (4H, m, *o*- and *m*-PhH); ^{13}C NMR δ (80 MHz), 17.1 (7-C), 32.7 (6-C), 35.7 (4-C), 36.8 (8-C), 44.4 (5-C), 49.9 (1-C), 125.6 (2-C), 125.7 (3-C), 127.5 (*o*-PhC), 128.4 (*m*-PhC), 137.1 (*p*-PhC), 139.2 (*ipso*-PhC) and 215.8 (9-C). MS (EI) m/z 212.

Methyl 6-oxo-2-phenyltricyclo[3.3.1.0^{2,7}]nonane-5-carboxylate 16. The cyclohexenone ester **8**, $n = 1$ (2.0 g) in acetonitrile (450 mL) was irradiated for 1.5 h. The solvent was removed *in vacuo* to give a viscous oil, which was purified by flash chromatography, and then dissolved in hexane/ether (9 : 1) and cooled to −50 °C. The precipitate formed was collected, and the process repeated several times. The combined precipitates (88 mg, 4.4%) were washed with the same solvent mixture at −50 °C, to give methyl 6-oxo-2-phenyltricyclo[3.3.1.0^{2,7}]-nonane-5-carboxylate **16**, mp 136–137 °C; ^1H NMR[29] δ (400 MHz) 1.69 (1H, d, $J = 10.0$, 8_{exo}-H), 1.75 (1H, m, 3_{exo}-H), 1.88 (1H, ddd, $J = 15.0$, 11.0, and 6.6, 3_{endo}-H), 2.25 (2H, m, 4_{exo}-H, 4_{exo}-H), 2.36 (1H, ddd, $J = 12.5$, 6.5, and 3.0, 9_{syn}-H), 2.55 (1H, m, 8_{endo}-H), 2.69 (1H, dd, $J = 12.5$ and 2.0, 9_{anti}-H), 3.05 (1H, q, $J = 6.5$, 1-H), 3.35 (1H, dd, $J = 6.5$ and 5.5, 7-H), 3.83 (3H, s, ester CH_3), 7.29 (1H, m, *p*-PhH), and 7.40 (4H, m, *o*- and *m*-PhH); ^{13}C NMR δ 29.9 (3-C), 31.0 (4-C), 33.9 (8-C), 35.2(9-C), 38.9 (1-C), 52.2 (ester CH_3), 55.1 (7-C), 55.9 (2-C), 126.2 (*o*-PhC), 126.6 (*m*-PhC), 128.6 (*p*-PhC), 143.9 (*ipso*-PhC), 172.0 (ester C═O), and 210.8 (6-C). Found: C, 75.40; H, 6.63%. $C_{17}H_{18}O_3$ requires C, 75.53; H, 6.71. MS (EI) m/z 270.

The filtrate from the isolation of **16** was concentrated to give an oil (20 mg), which was shown spectrscopically to be a mixture of the tricyclic ketone **16** and methyl 9-oxo-2-phenylbicyclo[3.3.1]non-2-ene-5-carboxylate **15**: ^1H NMR δ (400 MHz), 1.64–2.45 (7H, ms, 4_{endo}-H, 6_{exo}-H, 6_{endo}-H, 7_{exo}-H, 7_{endo}-H, 8_{exo}-H, 8_{endo}-H), 2.68 (1H, dd, $J = 19.2$, and 3.8, 4_{exo}-H), 3.49 (1H, s, 1-H), 3.80 (3H, s, ester CH_3), 6.29 (1H, t, $J = 3.7$, 3-H), and 7.30 (5H, m, *o*-, *m*-, and *p*-PhH). MS (EI) m/z 270.

Methyl 7-oxo-1-phenyltricyclo[4.2.2.0^{3,8}]decane-6-carboxylate 17. Methyl 2-oxo-4-phenyl-1-(3′-butenyl)cyclohex-3-ene-1-carboxylate **8**, $n = 2$ (1.0 g) in acetonitrile (450 mL) was irradiated for 14 h, the reaction being monitored by gc-ms. The solvent was removed *in vacuo* to give a dark viscous oil, which was purified by flash chromatography (hexane/ether, 9 : 1). The resulting oil was triturated with the same solvent mixture to give some solid, and the filtrate was cooled to −50 °C when more product precipitated. The solids were combined to give the tricyclic ketoester **17** (250 mg, 40%) as needles, mp 82–83 °C; ^1H NMR δ (400 MHz) 1.72 (1H, ddd, $J = 13.8$, 4.8 and 3.3, 9_{endo}-H), 1.86 (1H, m, 9_{exo}-H), 1.92 (1H, m, 4_{syn}-H), 2.12 (1H, m, 4_{anti}-H), 2.33 (1H, dd, $J = 12.6$, and 3.0, 2_{syn}-H), 2.43 (1H, ddd, $J = 14.6$, 6.0, and 3.0, 5_{syn}-H), 2.59 (2H, m, 10_{endo}-H and 5_{anti}-H), 2.81 (1H, ddd, $J = 14.6$, 6.0, and 3.0, 10_{exo}-H), 2.96 (2H, m, 3-H and 2_{anti}-H), 3.30 (1H. br d, $J = 9.5$, 8-H), 3.83 (3H, s, ester CH_3), 7.29 (1H, m, *p*-PhH), 7.40 (4-H, *o*- and *m*-PhH); ^{13}C NMR δ (80 MHz) 24.7 (4-C), 29.3 (3-C), 31.4 (10-C), 35.8 (5-C), 37.2 (9-C), 37.8 (2-C), 49.3(1-C), 51.2 (8-C), 52.3 (ester CH_3), 57.1 (6-C), 124.7 (*o*-PhC), 125.9 (*p*-PhC), 128.3 (*m*-PhC), 150.0 (*ipso*-PhC), 173.7 (ester C═O), and 213.9 (7-C). $C_{18}H_{20}O_3$ requires C, 76.03; H, 7.09. Found: C, 75.95; H, 7.00%. MS (EI) m/z 284. Crystals for X-ray analysis were grown from a hexane/ether solution (9 : 1) at 5° C, collected, washed with the same solvent at −50 °C, and dried *in vacuo* in a desiccator.

Methyl 11-oxo-3-phenyltricyclo[4.3.2.0^{3,10}]undecane-6-carboxylate (18). Methyl 2-oxo-1-(4′-pentenyl)-4-phenylcyclohex-2-ene-1-carboxylate **8**, $n = 3$ (1.0 g) 1n acetonitrile (450 mL) was irradiated for 17 h, the reaction being monitored by gc-ms. The solvent was removed *in vacuo* to give a dark viscous oil, which was purified by flash chromatography (hexane/ether, 9 : 1). The resulting oil was triturated with hexane/ether (9 : 1) to give some solid. The filtrate was cooled to −50 °C, when more solid precipitated. The combined solids were dried *in vacuo* in a desiccator to give the tricyclic ketoester **18** as needles (271 mg, 27%), mp 76–77 °C; ^1H NMR δ (400 MHz) 1.43 (1H, tt, $J = 12.5$, and 2.5, 9_{exo}-H), 1.80 (5H, m, 5_{exo}-H, 4_{endo}-H, 9_{endo}-H, 8_{exo}-H, and 8_{endo}-H), 2.05 (1H, dt, $J = 14.0$ and 3.3, 5_{endo}-H), 2.13 (2H, m, 4_{exo}-H and 7_{exo}-H), 2.55 (1H, m, 2_{endo}-H), 2.59 (1H, dd, $J = 13.0$ and 5.5, 7_{endo}-H), 2.69 (1H, dd, $J = 13.5$ and 8.0, 2_{exo}-H), 2.86 (1H, m, 1-H), 3.55 (1H, d, $J = 11.5$, 10-H), 3.74 (3H, s, ester-CH_3), 7.22 (4H, *o*- and *m*-PhH), and 7.33 (*p*-PhH); ^{13}C NMR δ (80 MHz) 19.5 (4-C), 24.4 (1-C), 27.4 (7-C), 28.9 (2-C), 29.0 (9-C), 33.4 (5-C), 36.2 (8-C), 43.6 (3-C), 52.2 (ester-CH_3), 55.6 (10-C), 58.6 (6-C), 125.2 (*o*-PhC), 125.9 (*m*-PhC), 128.4 (*p*-PhC) 149.8 (*ipso*-PhC), 174.6 (ester C═O), and 211.3 (11-C). Found: C, 76.40; H,7.39%. $C_{19}H_{22}O_3$ requires C, 76.48; H, 7.43. MS (EI) m/z 298. Crystals for X-ray analysis were obtained from a hexane/ether (9 : 1) solution.

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29 The assignment of *exo*, *endo*, *syn* and *anti* in **16** are counter-intuitive but in accordance with IUPAC and CAS practice.

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