

Photochemistry of substituted cyclic enones. Part 12.¹

Photocycloaddition of 3-phenylcyclopentenone and 3-phenylcyclohexenone to (*E*)- and (*Z*)-1-phenylpropene

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The quantum yields of adduct formation and isomerisation of (*E*)- and (*Z*)-1-phenylpropene by 3-phenylcyclopentenone **1** and 3-phenylcyclohexenone **2** have been measured by ¹H-NMR spectroscopy in solutions of d₆-benzene. The adducts formed for each photoreaction have been shown to be independent of the starting 1-phenylpropene isomer. For 3-phenylcyclopentenone **1**, a photostationary state of 32:68 (*E*)- to (*Z*)-1-phenylpropene is achieved during the course of the reaction. This isomerisation reaction may occur through reversion of triplet 1,4-biradical intermediates to ground state molecules or by an energy transfer process. However for 3-phenylcyclohexenone **2** isomerisation occurs only through reversion of triplet 1,4-biradical intermediates. The mechanism of photoadduct formation and that of the isomerisation reaction are discussed for both phenylenones.

Rate constants for quenching of the 3-phenylcyclopentenone **1** and 3-phenylcyclohexenone **2** triplet states by (*E*)- and (*Z*)-1-phenylpropene, **3** and **4**, in cyclohexane and benzene solutions have been recorded using laser flash photolysis. In cyclohexane at high quencher concentration, complex decay kinetics are observed consistent with observation of both the enone triplet state and either a triplet exciplex or 1,4-biradical intermediates.

Introduction

The [2+2] photoaddition reactions of cyclic enones with alkenes have been of general interest both from a mechanistic and a synthetic perspective for some time.²⁻⁴ Our investigations in this area have been concerned with the regiochemistry of the cycloadducts formed^{5,6} and with quenching and time-resolved studies of the intermediates involved.^{1,7} There is general agreement that triplet 1,4-biradicals are intermediates in these reactions, as was suggested by Bauslaugh,⁸ and that they may either collapse back to starting materials or proceed to give a cyclobutane adduct.⁹⁻¹¹

We have shown that 3-phenylcyclopentenone on photolysis with either (*E*)- or (*Z*)-1-phenylpropene gives rise to two adducts, 7-*endo*-methyl-5,6-*exo*-diphenylbicyclo[3.2.0]heptan-2-one **5** and 7-*exo*-methyl-5,6-*endo*-diphenylbicyclo[3.2.0]heptan-2-one **6**.¹² Only one regiochemistry is found but the

endo-diphenylbicyclo[4.2.0]octan-2-one **7**,¹² the regiochemistry of this reaction being the same as that of the reactions with 3-phenylcyclopentenone. In each product, the methyl and phenyl groups of the original alkene are *trans* to each other.¹²

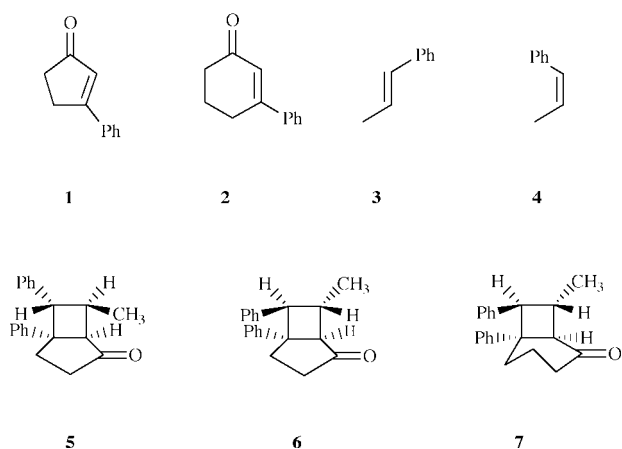
In this paper we report on the quantum yields of adduct formation and isomerisation for the reactions of 3-phenylcyclopentenone and 3-phenylcyclohexenone with both (*E*)- and (*Z*)-1-phenylpropenes. Our aim is to gain a better understanding of the mechanisms involved in these cycloaddition reactions, including whether the isomerisation proceeds *via* energy transfer or through biradical intermediates. Quenching rate constants for the phenylpropenes with both phenylenones have been determined in benzene and in cyclohexane. These values have been compared with quantum yields of isomerisation and adduct formation to yield kinetic data for the reversion and interconversion of the intermediates formed.

Experimental

Materials

(*E*)-1-Phenylprop-1-ene was purchased from Aldrich (Found: C, 91.28; H, 8.57. Calc. for C₉H₁₀: C, 91.47; H, 8.53%), and was found to be free of (*Z*)-isomer by ¹H-NMR. (*Z*)-1-Phenylprop-1-ene was prepared according to a procedure developed by Brown and Ahuja.¹³ This was purified by flash chromatography (silica gel, pentane) to give (*Z*)-1-phenylpropene (Found: C, 91.18; H, 8.60. Calc. for C₉H₁₀: C, 91.47; H, 8.53%). By ¹H-NMR the product was found to contain ~0.1% of the (*E*)-isomer and ~2% of 1-phenylpropane.

3-Phenylcyclopentenone and 3-phenylcyclohexenone were prepared as described previously.¹⁴ These enones were purified by vacuum sublimation (90 °C, 4 × 10⁻² mbar) and recrystallisation from ethyl acetate. Elemental analysis for 3-phenylcyclopentenone (Found: C, 83.35; H, 6.31. Calc. for C₁₁H₁₀O: C, 83.52; H, 6.37%) and 3-phenylcyclohexenone (Found: C, 83.52; H, 7.07. Calc. for C₁₂H₁₂O: C, 83.69; H, 7.02%) as well as the results of NMR and HPLC were consistent with pure compounds. Benzophenone was recrystallised from cyclohexane.



stereochemistry of the alkene is lost. By contrast, irradiation of a mixture of either (*E*)- or (*Z*)-1-phenylpropene with 3-phenylcyclohexenone affords only one product, 8-*exo*-methyl-6,7-

Diethyl ether was distilled over sodium with benzophenone as indicator. Isopentane (Aldrich, Spectroscopic grade), 96% ethanol (Merck), tetrahydrofuran (Reidel-de Haën, Chromosolv™ grade), cyclohexane (Aldrich, Spectroscopic grade), benzene (Aldrich, HPLC grade) and d_6 -benzene (Aldrich, 99+ atom%) were used without further purification.

Instrumentation

Nanosecond laser flash photolysis was carried out using a Lambda Physik EMG-50 XeCl excimer laser providing single pulses of duration *ca.* 15 ns and energies of 20 mJ, at 308 nm. The analysing light was provided by a 250 Watt Xe arc lamp in a cross beam configuration. The analysing beam was passed through the sample cell and then through an Applied Photophysics *f*/3.4 monochromator onto an R928 photomultiplier. The photomultiplier response was fed to a Tektronix TDS 380 digital oscilloscope. Solution concentrations were chosen with an absorbance of less than 0.8 at 308 nm and were degassed by three freeze–pump–thaw cycles. Transient UV–vis absorption spectra were obtained by recording the transient signal at successively increasing analysing wavelengths.

Triplet energies of the phenylenones were determined from their phosphorescence spectra in ethanol–diethyl ether–isopentane (2:5:5, v/v) (EPA) at 77 K. Spectra were recorded on a Perkin-Elmer MPF-44B fluorescence spectrometer with a 150 Watt Xe lamp and Hamamatsu R928 red sensitive photomultiplier. Phosphorescence decays monitored at 515 nm were recorded using the TDS 380 oscilloscope following laser excitation at 308 nm. Samples were contained in a 3 mm quartz cell in an Oxford Instruments DN704 cryostat cooled to 77 K.

Irradiation of solutions of **1** or **2** (8×10^{-2} mol dm⁻³) and 1-phenylpropene (8×10^{-2} mol dm⁻³) was achieved using 313 nm UV radiation from a Wotan HBO 500 Watt Xe lamp coupled to an Applied Photophysics M500 monochromator after passage through a water filter. The output of the Wotan HBO Xe lamp at 313 nm was determined by ferrioxalate actinometry according to the method of Hatchard and Parker¹⁵ and was performed before each irradiation.

Preliminary experiments on the photoaddition and isomerisation reactions were directly monitored by 400 MHz ¹H-NMR (Bruker DPX 400) in solutions of d_6 -benzene in an NMR tube.

Quantum yields were determined by irradiating a sample in a 1 cm quartz cuvette degassed by three freeze–pump–thaw cycles ($<4 \times 10^{-2}$ mbar). The de-aerated solution of phenylenone and 1-phenylpropene in d_6 -benzene was irradiated to ~5% conversion. Solutions were stirred during the course of the experiment and aliquots taken for analysis by NMR. Each value was determined three times.

Results

By following the photoreaction of a particular phenylenone and 1-phenylpropene using ¹H-NMR it is possible to detect simultaneously, at any time during the course of the reactions, the amount of starting materials, photoadducts and of 1-phenylpropene isomers. By irradiating in a 1 cm quartz cuvette at 313 nm, where neither the photoadducts nor the 1-phenylpropenes absorb, quantum yields for both photoadduct formation and photoisomerisation may be determined. As shown below the results encountered for 3-phenylcyclopentenone and 3-phenylcyclohexenone were found to differ considerably (Table 1).

Benzophenone (8×10^{-2} mol dm⁻³) was used as a high-energy sensitiser to follow the isomerisation of both (*E*)- and (*Z*)-1-phenylpropene (8×10^{-2} mol dm⁻³) to verify that our technique gave similar results to those in the literature.^{16,17} Irradiating samples at 313 nm in d_6 -benzene allowed determination of the quantum yields for each process. They were found to be 0.50 ± 0.02 for both isomers. In either case a photostationary state was achieved at a ratio of 35:65 for the

Table 1 Quantum yields (QYs) of adduct formation and isomerisation and photostationary states (PSS), for **1** (3-PCP) and **2** (3-PCH) with **3** (*E*-1-PP) and **4** (*Z*-1-PP), measured at room temperature in d_6 -benzene

Enone	Alkene	QY isom.	QY adduct	PSS (<i>E</i> : <i>Z</i>)
3-PCP	<i>Z</i> -1-PP	0.23 ± 0.02	0.021 ± 0.002	32:68
3-PCP	<i>E</i> -1-PP	0.16 ± 0.02	0.023 ± 0.002	32:68
3-PCH	<i>Z</i> -1-PP	0.20 ± 0.02	0.32 ± 0.02	47:53
3-PCH	<i>E</i> -1-PP	0.072 ± 0.005	0.21 ± 0.02	47:53

Concentrations of phenylenone and alkene (0.08 M), irradiating wavelength 313 nm.

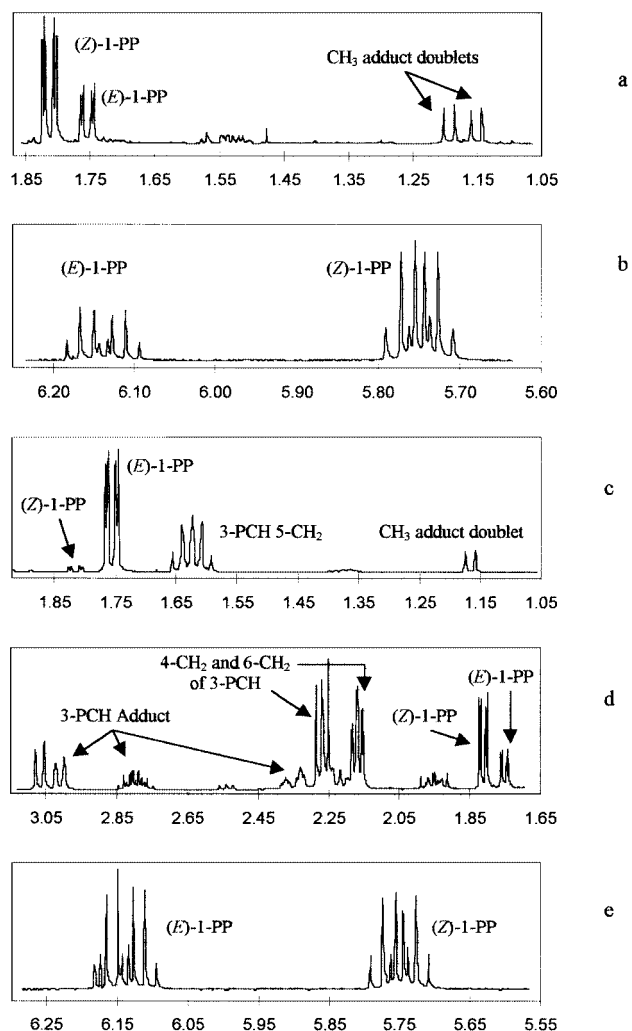


Fig. 1 Example 400 MHz ¹H-NMR spectrum of irradiated (313 nm) solutions in d_6 -benzene of (a) **1** and **4**, showing CH₃ doublet signals of adducts **5** and **6**, (b) **1** and **3**, at the photostationary state, (c) **2** and **3**, showing growth of the CH₃ doublet of adduct **7** and isomerisation of the 1-phenylpropenes, (d) **2** and **4**, showing the growth of signals from adduct **7** and (e) **2** with **3** and **4**, at the photostationary state.

(*E*)- and (*Z*)-isomers respectively. These results agree well with literature values, where the isomerisation process was followed by gas phase chromatography.^{16,17}

3-Phenylcyclopentenone (**1**)

Adduct formation. Upon irradiation of 3-phenylcyclopentenone, in the presence of either (*E*)- or (*Z*)-1-phenylpropene in benzene solution, two adducts have been identified, 7-endo-methyl-5,6-*exo*-diphenylbicyclo[3.2.0]heptan-2-one and 7-*exo*-methyl-5,6-*endo*-diphenylbicyclo[3.2.0]heptan-2-one, **5** and **6** respectively.¹² On irradiation in d_6 -benzene and monitoring by ¹H-NMR, the two adducts **5** and **6** are easily identified by their characteristic methyl doublets at δ 1.19 and at δ 1.15 (Fig. 1a).

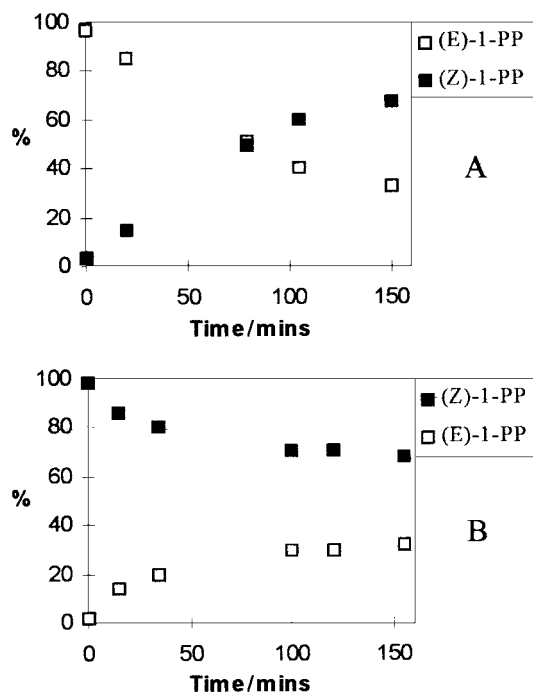


Fig. 2 Relative amounts of 1-phenylpropenes determined by $^1\text{H-NMR}$ following irradiation (313 nm) of **1** (0.08 M) with (A) **3** (0.08 M) and (B) **4** (0.08 M), in solutions of $\text{d}_6\text{-benzene}$.

The ratio of adducts formed was measured for both 1-phenylpropenes at very low conversion times to avoid the isomerisation reaction proceeding by more than 5% conversion of the starting alkene isomer. The two adducts were formed in a 53:47 ratio for **5** and **6** respectively. This ratio remained constant throughout the course of the reaction and was independent of the 1-phenylpropene isomer used as starting material. The quantum yields of adduct formation for 3-phenylcyclopentenone with (*E*)- and (*Z*)-1-phenylpropene were found to be 0.023 ± 0.002 and 0.021 ± 0.002 respectively.

Isomerisation. The isomerisation reaction was monitored by integration of the C-2 hydrogen peaks of the (*E*)- and (*Z*)-isomer at δ 6.14 and δ 5.75 respectively (Fig. 1b) and also by comparison of their methyl hydrogen signals at δ 1.76 and δ 1.81. Isomerisation was found to occur much faster than adduct formation for 3-phenylcyclopentenone. At low conversion times, the quantum yields for isomerisation for the (*E*)- and (*Z*)-1-phenylpropenes were 0.16 ± 0.02 and 0.23 ± 0.02 respectively. Due to the relatively large rates of isomerisation compared with that of adduct formation a photostationary state is achieved before ~15% of the starting enone is converted to adduct. The relative amounts of (*E*)- and (*Z*)-1-phenylpropene are plotted and shown to reach a 32:68 ratio irrespective of starting from either 100% of the (*E*)-isomer or from 100% of the (*Z*)-isomer (Fig. 2).

3-Phenylcyclohexenone (**2**)

Adduct formation. Irradiation of 3-phenylcyclohexenone in the presence of either (*E*)- or (*Z*)-1-phenylpropene in benzene has been shown to give only one adduct, 8-*exo*-methyl-6,7-*endo*-diphenylbicyclo[4.2.0]octan-2-one **7**.¹² Irradiating in $\text{d}_6\text{-benzene}$ and monitoring by $^1\text{H-NMR}$ the adduct formation could be followed by the growth of the methyl hydrogen doublet at δ 1.16 (Fig. 1c) as well as the hydrogens listed in Table 2 and shown in Fig. 1d. The quantum yields of adduct formation for 3-phenylcyclohexenone were found to be much larger than those for 3-phenylcyclopentenone. With (*E*)- and (*Z*)-1-phenylpropene values of 0.21 ± 0.02 and 0.32 ± 0.02 respectively, were recorded.

Table 2 $^1\text{H-NMR}$ spectral data for compounds **1** to **7**, measured in $\text{d}_6\text{-benzene}$ at room temperature

Compound			
1	2-H, t, δ 6.50	4-H, m, δ 2.3	5-H, m, δ 2.2
2	2-H, t, δ 6.57	4-H, m, δ 2.26	5-H, m, δ 1.62
3	1-H, d, δ 6.41	2-H, dq, δ 6.14	CH ₃ , d, δ 1.75
4	1-H, d, δ 6.53	2-H, dq, δ 5.75	CH ₃ , d, δ 1.81
5	1-H, d, δ 3.05	6-H, d, δ 3.41	CH ₃ , d, δ 1.19
6	1-H, d, δ 2.75	6-H, d, δ 3.25	CH ₃ , d, δ 1.15
7	1-H, d, δ 3.00	7-H, d, δ 3.06	8-H, m, δ 2.77
			CH ₃ , d, δ 1.18

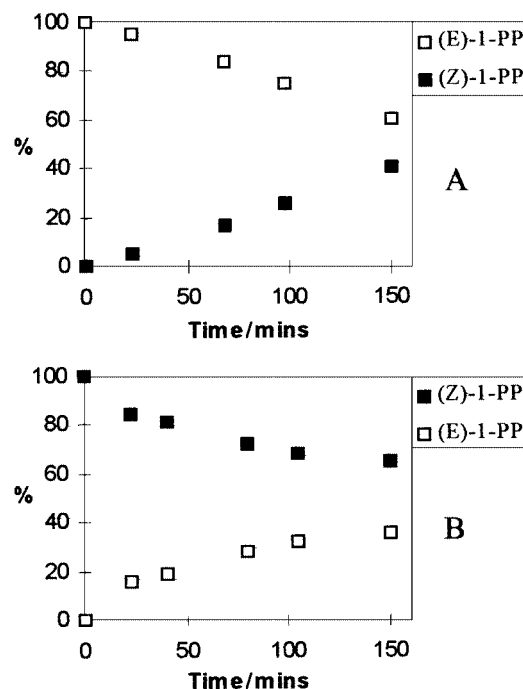


Fig. 3 Relative amounts of 1-phenylpropenes determined by $^1\text{H-NMR}$ following irradiation (313 nm) of **2** (0.08 M) with (A) **3** (0.08 M) and (B) **4** (0.08 M), in solutions of $\text{d}_6\text{-benzene}$.

Isomerisation. The isomerisation reaction of 1-phenylpropene was followed by integration of the C-2 and the methyl hydrogen peaks of the (*E*)- and (*Z*)-isomers as carried out previously. In the presence of 3-phenylcyclohexenone **2**, isomerisation of both alkenes was found to occur more slowly than adduct formation. This is in contrast to the results found for 3-phenylcyclopentenone **1**. The quantum yield of isomerisation measured at low conversion times for (*E*)-1-phenylpropene was determined as 0.072 ± 0.005 and that of (*Z*)-1-phenylpropene as 0.20 ± 0.02 . Since adduct formation is the dominant process for 3-phenylcyclohexenone, a photostationary state is not achieved during the course of the reaction. When starting with either 100% of the (*E*)- or (*Z*)-alkene, neither reaches equilibrium before the reactants are used up (Fig. 3). However when starting with close to an equimolar mixture of (*E*)- and (*Z*)-isomers a photostationary state is achieved at a ratio of 47:53 respectively, determined by integration of their C-2 hydrogen peaks (Fig. 1e).

Laser flash photolysis

The triplet state quenching rate constants of 3-phenylcyclopentenone **1** and 3-phenylcyclohexenone **2** by (*E*)- and (*Z*)-1-phenylpropene have been measured at room temperature in both degassed benzene and cyclohexane solutions and the results are summarised in Table 3.

Benzene solution. Throughout the quenching experiments in benzene the phenylenone concentration was held constant at

Table 3 Rate constants for quenching of **1** (3-PCP) and **2** (3-PCH) in cyclohexane and in benzene solution at room temperature, by **3** (*E*-1-PP) and **4** (*Z*-1-PP)

Quencher	Benzene		Cyclohexane	
	3-PCP	3-PCH	3-PCP	3-PCH
<i>Z</i> -1-PP	$(2.5 \pm 0.2) \times 10^8$	$(8.7 \pm 0.8) \times 10^6$	$(4.4 \pm 0.4) \times 10^8$	$(2.0 \pm 0.2) \times 10^7$
<i>E</i> -1-PP	$(8.9 \pm 0.8) \times 10^8$	$(2.4 \pm 0.2) \times 10^7$	$(2.1 \pm 0.2) \times 10^9$	$(5.0 \pm 0.4) \times 10^7$
Self	$(1.9 \pm 0.5) \times 10^8$	$<2 \times 10^6$	$(3.0 \pm 0.2) \times 10^8$	$<2 \times 10^6$

$\sim 2 \times 10^{-4}$ mol dm⁻³. This gave an absorbance at 308 nm for both enones **1** and **2** of ~ 0.6 . Extinction coefficients for **1** and **2** at 308 nm were determined to be 3385 dm³ mol⁻¹ cm⁻¹ and 3221 dm³ mol⁻¹ cm⁻¹ respectively. Rate constants were determined over a range of quencher concentrations up to 4×10^{-3} mol dm⁻³ for **1** and up to 4×10^{-2} mol dm⁻³ for **2**. The excited state of **1** was quenched efficiently in the presence of (*E*)- and (*Z*)-1-phenylpropene, giving values of $(8.9 \pm 0.8) \times 10^8$ and $(2.5 \pm 0.2) \times 10^8$ dm³ mol⁻¹ s⁻¹ respectively. The excited state of **2** was also quenched but by more than an order of magnitude less efficiently. Values of $(2.4 \pm 0.2) \times 10^7$ and $(8.7 \pm 0.8) \times 10^6$ dm³ mol⁻¹ s⁻¹ were measured for (*E*)- and (*Z*)-1-phenylpropene respectively. All traces decayed exponentially.

However in the absence of the alkene quencher, the traces no longer fit single exponential curves. χ^2 values of ~ 1.25 were observed for fits of experimental data for **1** to single exponential decays. This deviation from first order kinetics is less noticeable for compound **2**. Plots of the enone triplet decay rate against enone concentration show some curvature using these data, which leads to larger errors for the self quenching rate constants calculated. Slopes are found to be reduced with increasing enone concentration. However, for concentrations up to 2×10^{-4} mol dm⁻³ a value of $(1.9 \pm 0.5) \times 10^8$ dm³ mol⁻¹ s⁻¹ was found for **1** and a value less than 2×10^6 dm³ mol⁻¹ s⁻¹ was observed for **2**. Limiting lifetimes of 16 ± 4 μ s and 3.9 ± 0.2 μ s were determined for the triplet states of **1** and **2** respectively. The deviation from first order kinetics is discussed below.

Cyclohexane solution. For the quenching experiments in cyclohexane the phenylene concentration was kept constant at $\sim 6 \times 10^{-4}$ mol dm⁻³, leading to an absorbance at 308 nm for both phenylenones of ~ 0.45 . Extinction coefficients for **1** and **2** at 308 nm were found to be 657 dm³ mol⁻¹ cm⁻¹ and 777 dm³ mol⁻¹ cm⁻¹ respectively. Rate constants were determined over a range of quencher concentrations up to 1×10^{-3} mol dm⁻³ with **1**. Values of $(2.1 \pm 0.2) \times 10^9$ and $(4.4 \pm 0.4) \times 10^8$ dm³ mol⁻¹ s⁻¹ were recorded with (*E*)- and (*Z*)-1-phenylpropene respectively. These rate constants agree with those determined previously of $(2.2 \pm 0.4) \times 10^9$ and $(5.1 \pm 1.0) \times 10^8$ dm³ mol⁻¹ s⁻¹ for the (*E*)- and (*Z*)-isomer respectively.⁷ Above $\sim 2 \times 10^{-3}$ mol dm⁻³ of (*E*)-1-phenylpropene fits of the experimental data to a single exponential curve are very poor. However, the data does fit to a double exponential curve. The lifetime of one component has been found to be independent of both the enone and the alkene concentration. Whereas the second component was quenched by the alkene at a rate constant equal to that determined for quenching of the enone triplet state. The transient, which was not observed previously, has a lifetime of 2.5 μ s and is efficiently quenched in the presence of oxygen. This transient's absorption spectrum shows a maximum at 372 nm (Fig. 4) which is red shifted 12 nm from that of the 3-phenylcyclopentenone triplet absorption spectrum.¹⁸ It is clearly a product of the quenching reaction, probably retains triplet multiplicity and decays unimolecularly. We assume this transient to be either exciplex or triplet 1,4-biradicals arising from the phenylene and 1-phenylpropene.

For **2**, quenching rate constants were determined over a quencher concentration range up to 7×10^{-3} mol dm⁻³. Quenching rate constants of $(5.0 \pm 0.4) \times 10^7$ and $(2.0 \pm 0.2) \times$

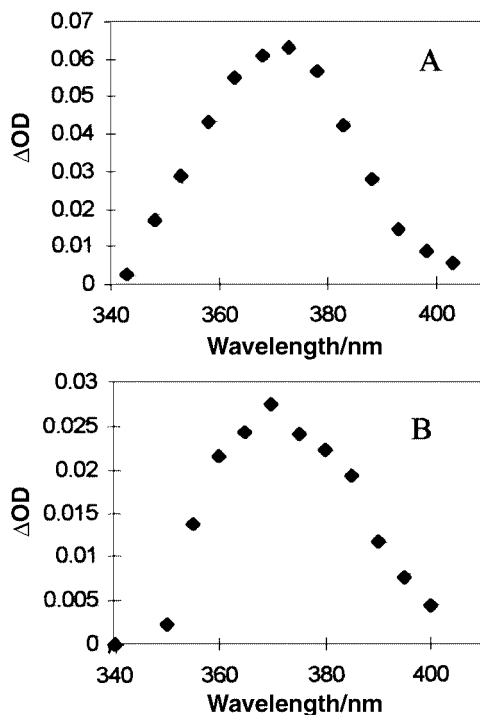


Fig. 4 Transient absorption spectra recorded following laser excitation of solutions of (A) 3-phenylcyclopentenone **1** and high concentration of 1-phenylpropene and (B) 3-phenylcyclohexenone **2** and high concentration of 1-phenylpropene, in cyclohexane.

10^7 dm³ mol⁻¹ s⁻¹ were found with (*E*)- and (*Z*)-1-phenylpropene respectively. Interestingly for both isomers the quenching rate constants observed in cyclohexane† are approximately twice those found in benzene solution. Double exponential behaviour is observed at increased concentration of 1-phenylpropene and the behaviour of the two components is similar to that observed for **1** in cyclohexane. On increasing the concentrations of alkene quencher still further, a single long-lived absorption trace is observed. This transient decays unimolecularly, has a lifetime of 3.2 μ s and is quenched efficiently in the presence of oxygen. It is red shifted by 18 nm to 370 nm in its absorption spectrum maximum (Fig. 4), compared to that of the 3-phenylcyclohexenone triplet state.⁷

Phosphorescence

The phosphorescence spectra of the phenylenones were recorded in glasses of ethanol–isopentane–diethyl ether (2:5:5, v/v) (EPA) at 77 K, and their triplet energies were determined from the 0–0 vibrational band peak maximum. Values of 249

† These quenching studies for 3-phenylcyclohexenone differ from those reported previously.⁷ The earlier determined values were recorded as single shot traces and the concentrations of phenylene and quencher which were used are lower, giving a larger signal to noise ratio. The errors reported previously were undoubtedly underestimated. The fact that no second component was observed is also due to the circumstances mentioned above and to the lower quencher concentrations used.

kJ mol⁻¹ and 225 kJ mol⁻¹ were recorded for 3-phenylcyclopentenone¹ and 3-phenylcyclohexenone respectively. The value for 3-phenylcyclohexenone agrees well with those reported previously by phosphorescence¹⁹ and photoacoustic calorimetry.²⁰ Phosphorescence lifetime measurements for 3-phenylcyclohexenone would not fit a single exponential. As has previously been observed for 3-phenylcyclopentenone,¹ fitting to a double exponential decay was necessary to give a good fit with experimental data for 3-phenylcyclohexenone. Lifetimes of 25 ms and 10 ms are observed in EPA glasses at 77 K, monitoring at 515 nm. In either pure ethanol or in diethyl ether-tetrahydrofuran (1:1, v/v) glasses at 77 K, single exponential phosphorescence decays have been observed. The lifetimes obtained respectively (24 ms and 10 ms), are similar to those recorded for the two components in EPA. As with 3-phenylcyclopentenone,¹ this is attributed to emission from the enone in different solvent sites within the EPA glass. Molecules in ether regions exhibiting a lifetime of 10 ms and those in ethanol regions are longer lived.

Discussion

Nature of the excited state of phenyl substituted enones

The phenyl substituted enones can be regarded as carbonyl derivatives of styrene. It is accepted that the triplet states of styrene and styrene derivatives adopt only the perpendicular conformation, except when the olefin is confined to planarity by a small ring.²¹ The relaxed triplet energies are also significantly lower than their planar spectroscopic triplet energies, (*i.e.* energies at ground state geometries).^{22,23} This energy gap is sensitive to constraints which affect the ability of the triplet state to twist about the double bond. No appreciable energy differences are observed for the highly constrained triplet states of 1-phenylcyclopentene or 1-phenylcyclohexene.²² The lifetimes of these triplet states are also increased remarkably due to their inability to access the perpendicular conformation of the ene component, thus preventing the near degeneracy of the ground and triplet surfaces. This arises as the energy of the ground state is expected to approach that of the triplet and possibly exceed it at the perpendicular conformation. This should also decrease spin-orbit coupling by maintaining the unpaired electrons in non-perpendicular orbitals.

Applying these considerations to cyclic enones, twisting about the C=C bond causes an increase in the energy of the ground state surface S_0 and a decrease in the triplet $\pi-\pi^*$ surface. This minimises the T_1-S_0 gap facilitating T_1-S_0 radiationless decay in a similar manner to that observed for the arylalkenes. As with the cyclic arylalkenes there is little difference in the relaxed and spectroscopic triplet energies²⁰ of **2** suggesting that its triplet is essentially planar. Therefore the triplet states of enones **1** and **2** are found to be much longer lived than those of the corresponding unsubstituted enones.^{24,25}

It has been suggested²⁰ that the triplet state of these 3-phenyl-substituted cyclic enones resembles that of a constrained substituted styrene rather than that of the cyclic enone because of the ability of the phenyl substituent to lower the energy of the planar triplet. Other parameters to be considered in determining the triplet energies of these compounds are torsion about the C=C bond and also pyramidalisation at the β -carbon atom which is also a significant relaxation mode on the triplet surface of the enone chromophore. These factors must be larger for the less constrained cyclohexenone **2** than for the smaller ring compound **1** giving rise to the lower lifetime and energy for enone **2**.

Phosphorescence

3-Phenylcyclohexenone **2** phosphorescence decays fit double exponential behaviour in EPA. As mentioned above this may be explained by solvent site effects. Two different single exponen-

Table 4 Time resolved emission data for **1** (3-PCP) and **2** (3-PCH), measured at 77 K

Comp.	Solvent	$(A_1/A_1 + A_2)$	τ_1/ms	$(A_1/A_1 + A_2)$	τ_2/ms
2	Ethanol	100	24	—	—
2	EPA	45	25	55	10
2	Diethyl ether-THF	—	—	100	10
1	Ethanol	100	57	—	—
1	EPA	58	59	42	23
1	Diethyl ether-THF	—	—	100	24

Decay traces fitted to the expression $A_1e^{-t/\tau_1} + A_2e^{-t/\tau_2}$.

tial decays are observed in both pure ethanol and diethyl ether-tetrahydrofuran (1:1, v/v) glasses at 77 K. Solvent site effects have been reported because of mixing of close lying $n-\pi^*$ and $\pi-\pi^*$ states. Such a situation is also expected for enones **1** and **2**. As previously proposed for indan-1-ones²⁶ the longer lived emission may arise from molecules H-bonded to the solvent and the short lived emission originates from molecules in a non-polar solvent cage. Comparison of the fraction of the recorded phosphorescence found in either solvent for 3-phenylcyclohexenone, 3-phenylcyclopentenone and related compounds¹ is consistent with the relative polarity of each compound. The more polar the phenylene the larger the degree of phosphorescence that is observed in ethanol glasses (Table 4). No phosphorescence is observed from the 1-phenylpropenes.²⁷ Indeed Crosby and co-workers²⁷ failed to detect any phosphorescence for a series of styrenes including 1-phenylcyclopentene either by direct irradiation or by triplet sensitisation, even at temperatures as low as 10 K in a nitrogen matrix.

Flash photolysis studies

These measurements provide evidence for quenching of the triplet excited state of both phenylenones. In both cases a second transient species has been detected in cyclohexane and specific solvent interactions with the enone triplet state in benzene have been observed.

The rate constants observed in benzene are all approximately half the values measured in cyclohexane implying that there might be an interaction between the solvent and the phenylene. It is possible that the benzene molecule solvates the phenylene by a stacking interaction. This will then hinder the approach of the alkene quencher, thus reducing its quenching rate constant. As the reduction in the rate constant is by a factor of two in all values determined, the strength of the interaction that causes it must be equal in each case. This interaction may also be the cause of the non-exponential triplet enone decays observed in the absence of quencher and the large errors encountered for the self quenching results in benzene.

In cyclohexane the quenching reaction of **1** or **2** by the 1-phenylpropenes produces a second species which decays unimolecularly and is deactivated by oxygen. A similar behaviour has been reported by Caldwell and co-workers²⁸ for the unsubstituted cyclopentenone self quenching reaction in acetonitrile. In that case this is attributed to direct detection of triplet 1,4-biradicals produced from the dimerisation reaction of cyclopentenone. He reports that laser flash photolysis gives rise to two transients, one of which is dependent on the enone concentration and a second species which is independent of the concentration of cyclopentenone, similar to the results observed for the phenylene-alkene reaction above. Direct observation of triplet 1,4-biradicals has also previously been described for other enone-alkene systems by photoacoustic calorimetry.²⁹

In our studies reported here with both phenylenones **1** and **2** the second transient species also fits a single exponential decay. The analysis of the products indicates that two biradicals must

be formed from **1**, so that if the observed transient is due to biradicals then both biradicals must decay with similar rates. Alternatively this transient species may be a triplet exciplex formed prior to biradical formation.

This triplet exciplex might react to form triplet biradicals but could also be capable of reversion to ground state starting materials and could account for the quantum yields of isomerisation observed. Evidence for a triplet exciplex intermediate has been proposed in the photocycloaddition reaction of 4,4-dimethylcyclopentenone to 1,1-diphenylethylene.³⁰ Whether the present species is an exciplex or biradicals will require different kinds of experimentation.

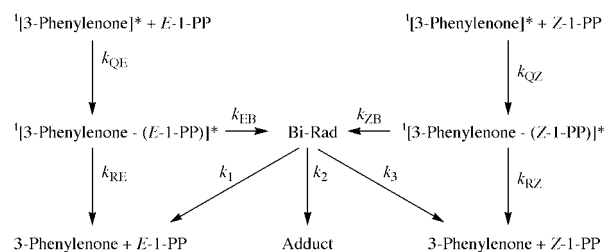
Quenching mechanism

It is evident from the triplet energies of 3-phenylcyclohexenone **2** (225 kJ mol⁻¹) and those of the (*E*)- and (*Z*)-1-phenylpropenes, (250 kJ mol⁻¹ and 275 kJ mol⁻¹ respectively),²² that energy transfer is energetically unfavourable and should not occur. Isomerisation in this case therefore is caused by reversion of 1,4-biradical intermediates to a ground state phenylenone and the 1-phenylpropene. The low quenching rate constants observed for 3-phenylcyclohexenone **2** would also suggest that isomerisation does not occur through energy transfer but rather through a chemical process. On the other hand the triplet energies of 3-phenylcyclopentenone **1** (249 kJ mol⁻¹) and (*E*)-1-phenylpropene are comparable and its isomerisation may involve both energy transfer and reversion of biradical species. In the case of (*Z*)-1-phenylpropene, although its triplet energy is higher than that of 3-phenylcyclopentenone, it has been shown to be capable of non-vertical triplet excitation transfer *via* single bond phenyl–vinyl torsion.^{23,31} Low frequency oscillations about this single bond at room temperature enable the molecule to explore more planar ground state conformations which will reduce spectroscopic triplet energies as a result of excited state stabilisation. A non-vertical transition is not observed when only double bond torsion is available. The dominant feature controlling non-vertical transitions is single bond torsion. The opportunity for phenyl–vinyl torsion to assist in non-vertical transfer requires a non-zero dihedral angle in the relaxed geometry of the ground state. Therefore (*E*)-1-phenylpropene behaves as a classical vertical acceptor. However, ground state (*Z*)-1-phenylpropene is a non-planar molecule and can behave as a non-vertical acceptor. The quenching rate constants observed for 3-phenylcyclopentenone by both 1-phenylpropenes are high and it is probable that the isomerisation can therefore take place by bond rotation in the triplet 1,4-biradical species or *via* the 1-phenylpropene triplet.

Photostationary state

The photostationary state was observed (NMR) for the 3-phenylcyclopentenone **1** induced equilibration of the (*E*)- and (*Z*)-1-phenylpropenes, and gave a ratio (*E*):(*Z*) of 32:68, reflecting the quenching rate constants observed for the two alkenes. However the photostationary state also depends on the decay ratio of the 1,4-biradical intermediates. The ratio can be estimated using the quenching rate constants and quantum yields of isomerisation of the (*E*)- or (*Z*)-1-phenylpropenes. Assuming the general mechanism suggested in Scheme 1, the calculation suggests an (*E*):(*Z*) ratio of 35:65 in good agreement with the experimental results. This calculation ignores the fact that two different 1,4-biradicals will be formed, and that there could be a possibility of an energy transfer route for alkene isomerisation.

Because the rate of adduct formation competes effectively with alkene isomerisation using **2**, the ratio of alkenes in the photostationary state is more difficult to determine accurately, but a ratio of 47:53 was obtained. Calculation as carried out above for **1** suggests an (*E*):(*Z*) ratio of 44:56, again in reasonable agreement with experiment.



Scheme 1

The agreement between the experimental and calculated photostationary states lends no information about the mechanism of the reaction, as both the quantum yield values and quenching rate constants determined are independent of the reaction mechanism. However the agreement between the two values does indicate that other processes, such as dimerisation and self quenching of the enone triplet states, are of minor importance under the conditions of the experiment. The photostationary state observed for the isomerisation reaction with a high energy photosensitiser such as benzophenone yields an (*E*):(*Z*) ratio of 35:65. The isomerisation process occurs only through energy transfer in this case. Comparison of this ratio to those found in the presence of **1** and **2** suggests that energy transfer is unimportant for **2** but may be quite effective in the case of **1**.

Reaction mechanism

The adducts formed from the 3-phenylenones and either 1-phenylpropene all have the original propene phenyl and methyl groups *trans* to each other. There are two possible explanations. Either the phenylenones **1** and **2** could sensitise both (*E*)- and (*Z*)-1-phenylpropenes initially but adduct formation would only be possible from the (*E*)-isomer. This appears to be ruled out in the case of the cyclohexenone for the reasons given above. Alternatively either alkene can react with the phenylenone to give 1,4-biradical(s). The biradical(s) can then either revert to the ground state molecules causing isomerisation or can form a photoadduct, but leading only to the *trans* adducts. This case will be discussed below.

The proposed mechanism for the reaction is shown in Scheme 1. Two non-interconvertible 1,4-biradicals may be formed, one with the methyl group of the alkene 'exocyclic' to the phenylenone ring and one adding 'endocyclically'. The possibility of energy transfer is not considered, though the triplet energies and quenching rate constants suggest that this may not be a valid assumption in the case of **1**. However, the mechanism suggested in Scheme 1 enables us to calculate the relative rates of how the 1,4-biradicals divide between adduct formation, isomerisation and reversion to starting materials. Furthermore, analysis of the kinetics leads to the conclusion that a precursor from which energy wastage competes with biradical formation is required to explain the results and the percentage of 1,4-biradicals formed can be determined based on the quantum yields of the various processes. These values are shown in Table 5. As the quantum yields of intersystem crossing for the phenylenones are expected to be close to unity, it is clear that in all reactions shown the dominant process is reversion to ground state molecules which occurs in preference to biradical isomerisation or adduct formation.

For both phenylenones, the quantum yield of isomerisation from the (*Z*)-1-phenylpropene is greater. This is expected as the equilibration of the 1,4-biradicals favours the (*E*)-isomer thermodynamically. This preference must dominate the kinetic advantage for reversion of the 1,4-biradicals to either the (*E*)- or (*Z*)-isomer and enone in order that agreement be reached with the experimentally determined values.

We have shown that for **1**, equilibration between the 1-phenylpropenes occurs at a faster rate than that of cycloaddition since

Table 5 Estimated fractional conversion to 1,4-biradicals from exciplexes of **1** and **2** with (*E*)- and (*Z*)-1-phenylpropene and relative rates of the 1,4-biradicals decay pathways, calculated by considering quantum yield values for each process in the general mechanism shown in Scheme 1

Cmpd.	$k_{EB'}/(k_{EB} + k_{RE})$	$k_{ZB'}/(k_{ZB} + k_{RZ})$	$k_1/(k_1 + k_2 + k_3)$	$k_2/(k_1 + k_2 + k_3)$	$k_3/(k_1 + k_2 + k_3)$
1 ^a	52.8%	69.9%	57.8%	5.3%	36.9%
2	46.7%	85.6%	31.5%	51.4%	17.1%

^a For **1** this analysis may be incorrect as energy transfer may be operative.

the quantum yields of adduct formation are small. Only ~5% of the 1,4-biradicals formed convert to adducts. Adducts are formed with quantum yields that are approximately equal whether starting with the (*E*)- or (*Z*)-1-phenylpropene. It has been argued that the equal ratios of adducts formed from the photocycloaddition reaction of *cis*- or *trans*-anethole with fumarodinitrile,³² similar to that which we observe for (*E*)- and (*Z*)-1-phenylpropene with **1**, may be caused by the approach of the alkene to form biradicals.

Ring-fusion stereochemistry

In the general case of cyclohexenones both *cis*- and *trans*-fused adducts are formed and in most cases, even with steroid enones, formation of adducts with *trans*-fused ring junctions is preferred.³³ This selectivity must have a kinetic rather than a thermodynamic basis, since the *cis*-fused adduct is the most stable.

The excited state of cyclohexenones which leads to adducts is a highly twisted $^3\pi-\pi^*$ state. If such a species were to interact directly with ground state alkenes, *trans*-fused adducts would be produced only if the cycloaddition reaction of this intermediate were competitive with relaxation of the biradical to its equilibrium geometry. However for **2** with a variety of alkenes no evidence for *trans*-fused adducts is observed.^{34,35} This is not surprising as in the triplet state of **2** no twisting about the C=C bond is expected and also the biradical formed prior to ring closure, which is stabilised by the phenyl group, will be capable of isomerisation to the relaxed geometry within this transient's lifetime. Therefore in all adducts formed **5–7** *cis*-fused ring junctions are observed.

Regiochemistry

The regiochemistry of the photocycloaddition reactions of cyclopentenones or cyclohexenones with alkenes is determined by the manner in which the triplet 1,4-biradicals partition between fragmentation to give ground state starting materials and closure to give products. Therefore their relative rates of formation are not the only factor involved. The regiochemistry of the 1,4-biradical forming step has been modelled by the $\pi-\pi^*$ triplet of acrolein.³⁶ This model suggests that the polarity of the alkene directs the attack of the enone 2- or 3-position onto the less substituted end of the alkene, which is in contrast to diradical trapping experiments which indicate no selectivity in α or β attack on the enone.^{9,10} If addition to the more substituted end of the alkene does occur, these intermediates revert rapidly and exclusively to ground state enone and alkene and take no part in cycloadduct formation. The authors do not distinguish between steric or electronic factors in causing this selectivity.

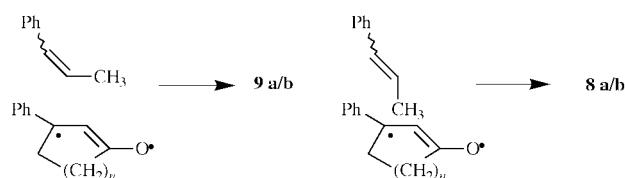
Substitution effects at the 2- and 3-position of cyclic enones have been examined by Weedon.^{9,10} The results are rationalised by considering the carbon at the 2-position of the enone triplet and the radical centre of the cyclic ketone to be planar and considering a pyramidalised carbon at the 3-position of these intermediates. The triplet lifetimes and energies of 2- and 3-substituted cyclic enones are in good agreement with this suggestion.²⁰ Methyl substitution at the 3-position of the enone has

little or no effect on either the relative rates of formation of the various 1,4-biradicals or on the manner in which they are distributed between reversion to starting materials and adduct formation. However, 2-methyl substitution, due to the increased steric effects for the planar radical, slows formation of biradicals in which the alkene is bonded to the 2-position and inhibits closure of products formed by bonding of the alkene to the 3-position of the enone.

The phenyl group in enones **1** and **2** affects the geometries of their triplets greatly. It is suggested that radical centres formed at either the 2- or 3-position of these enones will be planar, in contrast to those previously discussed. Therefore by analogy, in **1** or **2** where a planar 3-position is suggested, substitution by the phenyl group will cause steric effects which will slow formation of biradicals formed by initial bonding at the 3-position and will prevent cycloadduct formation in the biradical which requires further bonding of the alkene to the 2-position of the enone.

Initial bond formation. The first bond to be formed between ene and enone will be such as to give stable biradicals. As a radical is stabilised by a phenyl group to a greater extent than by a carbonyl group, both centres in the biradical will be benzylic in nature.³⁷ This requires the initial bond to be formed between the 2-position of the styrene side chain and the 2-position of the excited enone, thus controlling the regiochemistry of any products formed in the reactions. Evidence for the same regiochemistry has been observed for the cycloaddition reactions of *cis*- or *trans*-anethole to fumarodinitrile.³² Biradicals formed which lack the benzylic stabilisation of one radical centre have been ruled out by thermodynamic arguments.

Furthermore, the geometry of the transition state, in the formation of this bond requires that the ene double bond and the 1,2-bond of the excited enone molecule must lie in the same plane (Fig. 5). The (*E*)-1-phenylpropene can give rise to two different biradicals **8a** and **9a**, while the (*Z*)-1-phenylpropene affords **8b** and **9b**. **8a** and **8b** with the '*endo*'-CH₃, are different conformers of the same biradical, while **9a** and **9b** with an '*exo*'-CH₃ are also conformers of a different biradical. In the case of 3-phenylcyclopentenone **1**, **8a/b** and **9a/b** can all be



formed with no great steric strain, but in the case of 3-phenylcyclohexenone **2**, there is considerable steric strain introduced forming the '*endo*'-methyl biradical. This interaction between the ene methyl and 4- and 6-axial hydrogens in the cyclohexenone could result in slower rates of formation and in a higher rate of return to ene and enone. The '*exo*' CH₃ biradical, **9a/b** does not suffer from these steric interactions. This would account for the formation of products from **8** and **9** in the five membered enone case and only from **9** in the six membered enone.

Second bond formation. The formation of this bond must involve intersystem crossing of the triplet biradical and the singlet state. The stereoselectivity of photocycloaddition reactions of 1,4-biradicals has been rationalised by the preferred geometry at which triplet 1,4-biradicals undergo this type of intersystem crossing.^{38,39} Spin-orbit coupling which is assumed to be the most important contribution for determining the intersystem crossing rate is strongly dependent on the distance between the radical centres.⁴⁰ The angle between the p-orbitals at the radical centres is approximately orthogonal for maximum

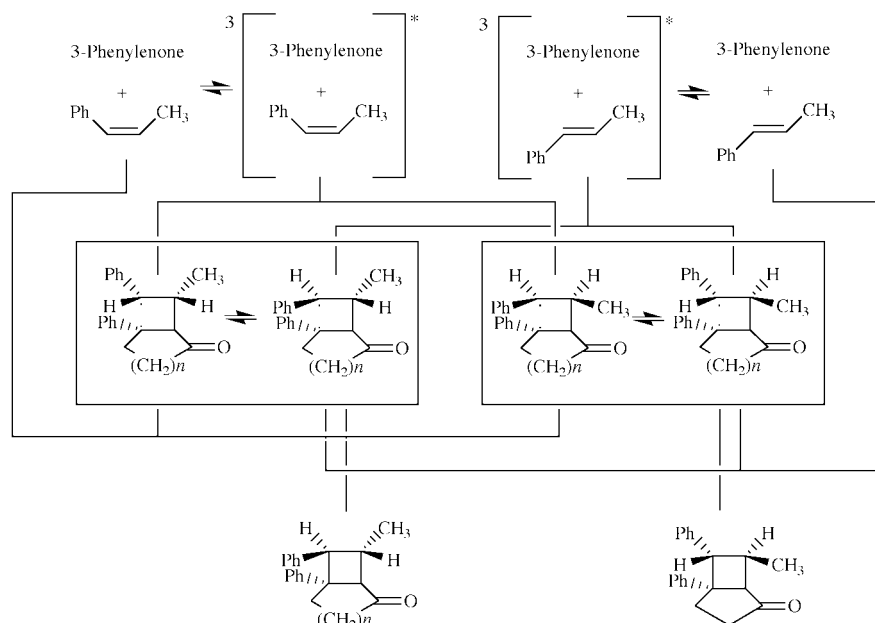
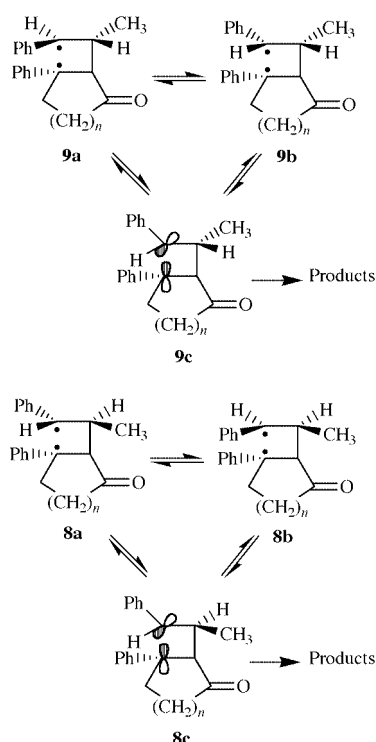


Fig. 5 Preferred conformations of the reactants and of the 1,4-biradical intermediates during initial bond formation.



spin-orbit coupling. This would require the 'endo'-biradical **8** to adopt the conformation **8c**, and the 'exo' **9** conformation **9c**. In both **8c** and **9c**, the phenyl group is pointing away from the rest of the molecule. The alternative conformations with the phenyl group 'endo' are impossible for steric reasons. The new conformation **8c** could be formed from either conformation **8a** or **8b** and hence from either (*E*)- or (*Z*)-alkene as inside the lifetime of these 1,4-biradicals rotation of the C–C single bond is possible. Similarly conformation **9c** could be derived from either alkene. Therefore the product stereochemistry should represent to a certain degree the geometry of the triplet 1,4-biradical during intersystem crossing.

The formation of the second bond can involve either lobe of the p-orbital at the side chain benzylic centre and the lobe favoured will be that which minimises steric repulsions. If the

side chain methyl and phenyl groups were to finish up *cis* in the products, then there would be considerable interactions between these groups in the transition state. Accordingly, products where the two substituents are *trans* to each other are preferred, as found in practice.

Conclusions

The combination of transient spectroscopic methods and quantum yield determinations has allowed us to gain considerable information about the mechanism of the formation of adducts between 3-phenylcycloalkenones and 1-phenylpropene, and the sensitised isomerisation of the olefin. The cyclopentenone **1** and cyclohexenone **2** compounds show different behaviour due both to the lower energy of the excited state of **2** compared to that of **1** and to differing steric effects of the phenyl group in reactions of the biradicals.

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