Photochemistry of Substituted Cyclic Enones. Part 7.[1] Flash Photolysis of 3-Phenylcyclopent-2-enones and 3-Phenylcyclohex-2-enone

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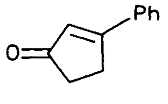
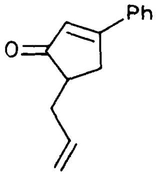
The spectra and lifetime of the triplet states of 3-phenylcyclopent-2-enone, 3-phenyl-5-(prop-2-enyl)-cyclopent-2-enone, and 3-phenylcyclohex-2-enone have been measured by laser flash photolysis (λ_{exc} 308 nm). The lifetimes of the triplet state of the 3-phenyl-substituted enones are considerably longer than those reported for the unsubstituted cyclo-enones. Rate constants for the quenching of these triplet states by oxygen, (*Z*)- and (*E*)-1-phenylprop-1-ene, (*Z*)- and (*E*)-penta-1,3-diene, cyclohexene, and 2,3-dimethylbutene are recorded.

Over the years we have been interested in the photochemical [2 + 2] cycloaddition reactions of 5-allyl-3-arylcyclopentenones[2,3] and we have explored the effect of alkyl and aryl substituents in the allyl side chain on the reaction. This suggested that we should examine more closely the nature of the excited state of 3-phenylcyclopent-2-enone (**1**),[4] 3-phenyl-5-(prop-2-enyl)cyclopent-2-enone (**2**) and, for comparison purposes, 3-phenylcyclohex-2-enone (**3**), using the technique of laser flash photolysis. Phosphorescence studies have already been reported on 3-phenylcyclopent-2-enone,[5] but no flash photolysis studies of the excited state in fluid solution have been reported for phenyl-substituted cyclic enones, although studies on unsubstituted cyclopentenone and cyclohexenone have been carried out.[6]



(**1**)



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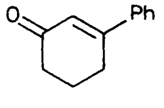

(**3**)

Results

Upon laser flash photolysis in deoxygenated cyclohexane solution, each of the three enones studied gave rise to a single transient species which decayed according to first-order kinetics with lifetimes in the microsecond region. In each case, the spectrum of the excited state was measured and found to be similar in shape to that already reported for compound (**1**)[4] with λ_{max} in the region 350–370 nm (Table 1). In the case of 3-phenylcyclopent-2-enone (**1**), the excited state spectrum was also measured in ethanol; this showed a slight shift in the λ_{max} to 367 nm, and considerable broadening of the spectrum towards longer wavelengths. In aerated solutions, the lifetimes of the transients of all three enones are markedly reduced. The rate constants for quenching by oxygen (Table 2) were obtained from measurements in which an oxygen concentration of 2.3×10^{-3} mol dm^{-3} in cyclohexane at 25 °C is assumed.[7] Such efficient quenching by oxygen (approximately diffusion controlled) is consistent with the transient species being triplet excited states. Further evidence for this comes from our observation that the species formed from (**1**) which exhibits the transient absorption at 360 nm has identical decay kinetics to that of the phosphorescence at 85 K in ether–isopentane–ethanol (EPA) glass, indicating that the same excited state is responsible for both.

Table 1. Band maxima in absorption spectra of ground- and triplet-excited states, and lifetimes of triplet-excited states in cyclohexane solution.

	Ground state		Excited state	
Compound	λ_{max}/nm	log ε	λ_{max}/nm	τ^a/μs
(**1**)	274	4.29	360	20
(**2**)	275.5	4.32	362	0.9
(**3**)	271	4.27	352	2.0

[a] Extrapolated to infinite dilution.

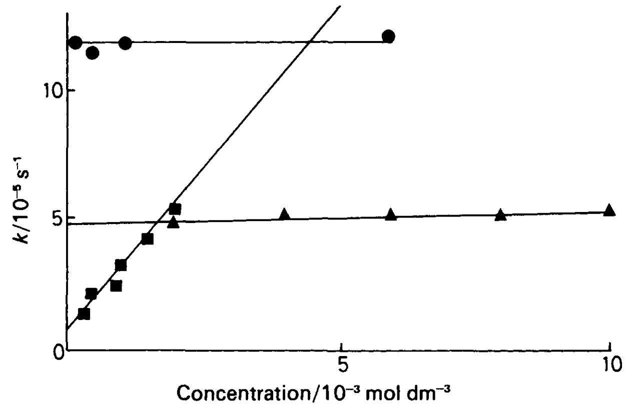

Figure. Dependence of the observed rate constant for decay of the triplet states for enones (**1**)–(**3**) as a function of their concentration in cyclohexane solution: ■, 3-phenylcyclopent-2-enone (**1**); ●, 3-phenyl-5-(prop-2-enyl)-cyclopent-2-enone (**2**); ▲, 3-phenylcyclohex-2-enone (**3**).

The lifetime of the transient species formed from (**1**) was strongly dependent on the concentration of enone, indicating that there is self-quenching. The rate constant for this process was determined as $(2.5 \pm 0.2) \times 10^8$ and $(1.7 \pm 0.2) \times 10^8$ dm^3 mol^{-1} s^{-1} in cyclohexane and ethanol, respectively. For 3-phenyl-5-(prop-2-enyl)-cyclopent-2-enone (**2**) and 3-phenylcyclohex-2-enone (**3**) the transient lifetimes were also concentration dependent, although to a much smaller extent than for (**1**). Here the self-quenching rate constants in cyclohexane were $(2.3 \pm 0.9) \times 10^7$ and $(1.0 \pm 0.2) \times 10^7$ dm^3 mol^{-1} s^{-1} for (**2**) and (**3**) respectively (Figure). By extrapolation, transient lifetimes at infinite dilution could be estimated as 20, 0.9, and 2 μs for (**1**), (**2**), and (**3**), respectively. In earlier studies with unsubstituted cyclopentenone and cyclohexenone,[6] self-quenching

Table 2. Rate constants for quenching of triplet-excited states of compounds (1)–(3) in cyclohexane solution.

	k/dm^3 mol^{-1} s^{-1}		
Enone quencher	**(1)**	**(2)**	**(3)**
(Z)-1-Phenylpropene	$(5.1 \pm 0.2) \times 10^8$	$(4.2 \pm 0.2) \times 10^8$	$(7.4 \pm 0.6) \times 10^7$
(E)-1-Phenylpropene	$(2.2 \pm 0.1) \times 10^9$	$(1.6 \pm 0.1) \times 10^9$	$(7.0 \pm 2.0) \times 10^7$
(Z)-Penta-1,3-diene	$(5.3 \pm 0.5) \times 10^9$	$(3.5 \pm 0.2) \times 10^9$	$(4.6 \pm 0.3) \times 10^8$
(E)-Penta-1,3-diene	$(3.1 \pm 0.1) \times 10^9$	$(3.5 \pm 0.1) \times 10^9$	$(3.2 \pm 0.5) \times 10^8$
Cyclohexene	$(1.1 \pm 0.1) \times 10^7$	$(7.1 \pm 0.5) \times 10^6$	$< 10^6$
2,3-Dimethylbut-2-ene	$(7.1 \pm 0.3) \times 10^6$	$(4.7 \pm 0.2) \times 10^6$	$< 10^6$
Oxygen	1.9×10^9	1.6×10^9	2.7×10^9
Self	$(2.5 \pm 0.2) \times 10^8$	$(2.3 \pm 0.9) \times 10^7$	$(1.0 \pm 0.2) \times 10^7$

has been ascribed to the interaction of an excited state enone with a ground-state enone molecule, yielding either a dimeric photoproduct, or two ground state enone molecules.[8,9] The same processes would be available to (1), (2), and (3). The differences obtained for the self-quenching rates obtained for (1) and (3) may be explained in terms of a very twisted excited state in the latter. The small self-quenching rate for (2) suggests that the allyl side chain prevents two molecules of (2) achieving the correct geometry for intermolecular quenching.

Quenching experiments with a variety of species of varying triplet energies, ranging from 238 to 293 kJ mol^{-1} were undertaken (Table 2). Simple alkenes, the triplet energies of which are not known but are assumed to be relatively high, were also employed in the quenching studies. Throughout the quenching experiments, the enone concentration was held constant at 10^{-4} mol dm^{-3}. Quenching rate constants were determined over a range of quencher concentrations up to 10^{-3} mol dm^{-3} for the more efficient quenchers, and up to 5×10^{-2} mol dm^{-3} for the simple alkenes. In degassed cyclohexane solutions of (1) and (2), the excited states were quenched efficiently in the presence of (E)- and (Z)-penta-1,3-diene (E_T 238 and 247 kJ mol^{-1}, respectively)[10] and (E)-1-phenylpropene (E_T 251 kJ mol^{-1}).[11] The transient arising from the excitation of (3) was also quenched by these species, but at about one order of magnitude less efficiently. For all three enones, the (Z)-1-phenylpropene (E_T 293 kJ mol^{-1})[12] was a less effective quencher. The rate constants for quenching with cyclohexene and 2,3-dimethylbut-2-ene were very low for the enones; in the case of 3-phenylcyclohexenone this quenching rate constant was less than 10^6 cm^3 mol^{-1} s^{-1}.

Discussion

The Excited State.—3-*Phenylcyclopentenone* (1). The absorption ground-state spectrum is dominated by the $\pi\rightarrow\pi^*$ transition at 274 nm (cyclohexane), and no clearly resolved $n\rightarrow\pi^*$ transition is observed. Results from quenching experiments with oxygen and other known triplet quenchers, along with the results previously reported from low-temperature phosphorescence studies[4,5] indicate that the transient species arising from 308 nm laser flash photolysis of the 3-phenylcyclopentenone is the triplet excited state. Given the absorption data, and the larger singlet–triplet splitting for the $\pi\rightarrow\pi^*$ state, it is expected that the triplet state will have a $\pi\rightarrow\pi^*$ configuration as previously suggested.[5] The lack of evidence for efficient hydrogen atom abstraction from either ethanol or cyclohexane at room temperature ($k_q < 10^4$ dm^3 mol^{-1} s^{-1}) is also consistent with the excited state having $\pi\rightarrow\pi^*$ rather than $n\rightarrow\pi^*$ character. Other phosphorescence studies on rigid alkyl substituted cyclopentenones[13] have assigned long-lived emissions to the lowest $\pi\rightarrow\pi^*$ triplet state.

A lifetime of approximately 20 μs in dilute solutions of the excited state from (1) is considerably longer than that of cyclopentenone itself for which Bonneau[6] found two transients having lifetimes of 30 and 45 ns, respectively, after excitation in cyclohexane solution. Earlier quenching studies showed that the second species is apparently formed from a precursor which could not be directly observed but which had a lifetime of >20 ns and a self-quenching rate constant of 1.2×10^9 dm^3 mol^{-1} s^{-1}.[6] These values are similar to those derived by Wagner and Bucheck[8] for the reactive species involved in photodimerization. A twisted form of the triplet state has been proposed for the τ = 30 ns transient species. The much longer lifetime found for (1) may be due to the fact that the phenyl group may conjugate with the excited enone species, and inhibit twisting. In addition any twisting in the excited state will bring the bulky phenyl group into closer proximity with the 4- and 5-methylene groups, and steric repulsion will come into play.

3-*Phenyl*-5-(*prop*-2-*enyl*)-*cyclopent*-2-*enone* (2). Apart from the lifetime and the self-quenching results, the behaviour of the excited state of (2) closely parallels that of (1) in both absorption and quenching studies. The relatively short lifetime can be explained by the intramolecular self-quenching reaction between the excited-state enone and ground-state ene to give either their ground states, or the cage ketone.[2] The decrease in transient absorption on repeated flashing is consistent with the latter process. As with the parent enone (1), twisting in the excited state would be inhibited by the phenyl group.

3-*Phenylcyclohexenone* (3). Although the lifetime of this transient is not as long as that of the corresponding cyclopentenone (1), it is markedly longer (τ = 2 μs) than the transient derived from unsubstituted cyclohexenone (τ = 25 ns in degassed cyclohexane)[6] and indeed from other cyclohexenones.[6,13–17] It is now recognized that two types of behaviour of the triplet excited states of cyclic enones may be distinguished.[17] The first, which have very short lifetimes, include unconstrained cyclohexenones (*e.g.* 4,4-dimethylcyclohexenone), while the second, which have longer lifetimes, includes cyclopentenone, 3-methylcyclohexenone and other constrained systems. The first group can afford a very twisted excited state, while in the second group, such twisting is inhibited. For enone (3) the presence of the phenyl group will cause considerable 1,3-interactions in the twisted conformation, and therefore (3) is expected to behave like other members of the second group proposed by Schuster *et al.*[17] As with (1) the extra stability of the excited state of (3) compared with that of other cyclohexenones may be attributed in part to conjugation with the phenyl ring.

Quenching Studies.—Schuster and co-workers have recently presented a series of papers on the interaction of cyclic enones and alkenes.[14,15,17] For flexible enones such as 4,4-dimethylcyclohexenone it was found that the triplet state observed on flash photolysis was not quenched by alkenes but that cycloaddition occurred from a precursor excited state. For cyclopentenone and the constrained cyclohexenones it was found that the triplet excited state observed by flash photolysis was indeed quenched by the alkene but there was no correlation between the effect of alkene concentration on the triplet lifetime and the quantum efficiency of the addition reaction.[18] The authors concluded that exciplexes are not involved in these intermolecular [2 + 2] photocycloadditions. Furthermore, they demonstrated that there is no triplet energy transfer from cyclopentenone, 3-methylcyclohexenone and other constrained cyclic enones and electron deficient alkenes (*e.g.* acrylonitrile). Our quenching experiments with electron-rich alkenes provide a contrast. The quenchers can be divided into two sets; those that quench with an approximately diffusion-controlled rate constant [(*E*)- and *Z*)-penta-1,3-diene and (*E*)-1-phenylpropene] and those which are less efficient. With the first group, the efficient quenching would suggest that it is occurring *via* an energy transfer process. Indeed we have shown by NMR monitoring that isomerization of (*E*)-1-phenylpropene occurs at a faster rate than cycloaddition when a solution of the alkene and 3-phenylcyclopentenone are irradiated with ultraviolet light. Such isomerization is consistent with energy transfer. The second set of quenchers may operate through a chemical process and may involve an exciplex and biradical species, which could then form a photoproduct (or photoproducts) or revert to two ground-state molecules. At some stage, electron spin inversion has to occur for bonding to occur.

In conclusion, the presence of a phenyl group in the 3-position of cyclic enones leads to a shift of the triplet excited state absorption into the near-UV and a considerable lengthening of its lifetime. This facilitates the use of these compounds for use as mechanistic probes and our current work is aimed at exploiting this.

Experimental

3-Phenylcyclopent-2-enone,[18] 5-(prop-2-enyl)-3-phenylcyclopent-2-enone,[3] and 3-phenylcyclohex-2-enone [18] were prepared by literature procedures. Cyclohexane was BDH Spectrosol grade.

Nanosecond flash photolysis was carried out using a XeCl excimer laser for excitation and a Xe-arc lamp as monitoring source in a cross-beam configuration. Further details have been published earlier.[19] Low-temperature experiments were performed using an Oxford Instruments DN704 cryostat with the sample dissolved in ethanol–isopentane–diethyl ether (2:5:5 v/v) (EPA) in a square 1 cm cuvette.

References

1 Part 6. M. T. M. Clements and T. B. H. McMurry, *Can. J. Chem.*, 1987, **65**, 1810.

2 I. D. Cunningham, T. B. H. McMurry, M. P. Napier, and S. N. Rao, *J. Chem. Soc., Perkin Trans. 1*, 1986, 1235.

3 M. T. M. Clements, R. C. Cathcart, I. D. Cunningham, T. B. H. McMurry, and S. N. Rao, *J. Chem. Res.*, 1984, (*S*) 223; (*M*) 2060.

4 Preliminary communication, J. M. Kelly, T. B. H. McMurry, and D. N. Work, *J. Chem. Soc., Chem. Commun.*, 1987, 280.

5 M. Magnifico, E. J. O'Connell, A. V. Fratini, and C. M. Shaw, *J. Chem. Soc., Chem. Commun.*, 1972, 1095.

6 R. Bonneau, *J. Am. Chem. Soc.*, 1980, **102**, 3816; T. D. Goldfarb, *J. Photochem.*, 1978, **8**, 29.

7 S. L. Murov, 'Handbook of Photochemistry,' Marcel Dekker, 1973, New York, p. 89.

8 P. J. Wagner and D. J. Bucheck, *J. Am. Chem. Soc.*, 1969, **91**, 5090.

9 R. O. Loutfy and P. de Mayo, *J. Am. Chem. Soc.*, 1977, **99**, 3559.

10 J. A. Barltrop and J. D. Coyle, 'Excited States in Organic Chemistry,' Wiley, Chichester, 1975, p. 130.

11 A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, 1965, **43**, 2129.

12 R. A. Caldwell, G. W. Sovocool, and R. J. Peresie, *J. Am. Chem. Soc.*, 1973, **95**, 1496.

13 R. L. Cargill, W. A. Bundy, D. M. Pond, A. B. Sears, J. Saltiel, and J. Winterle, *Mol. Photochem.*, 1971, **3**, 123.

14 D. I. Schuster, R. Bonneau, D. A. Dunn, J. M. Rao, and J. Joussot-Dubien, *J. Am. Chem. Soc.*, 1984, **106**, 2706.

15 D. I. Schuster, P. B. Brown, L. J. Capponi, C. A. Rhodes, J. C. Scaiano, P. C. Tucker, and D. Weir, *J. Am. Chem. Soc.*, 1987, **107**, 2355.

16 N. J. Pienta, *J. Am. Chem. Soc.*, 1984, **106**, 2704.

17 D. I. Schuster, G. E. Heibel, P. B. Brown, N. J. Turro, and C. B. Kumar, *J. Am. Chem. Soc.*, 1988, **110**, 8261.

18 D. G. Farnum, A. Mostashari, and A. A. Hagedorn, *J. Org. Chem.*, 1971, **36**, 698.

19 J. M. Kelly, W. J. van der Putten, and D. J. McConnell, *Photochem. Photobiol.*, 1987, **45**, 167.

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