Steady state and laser flash photolysis of acenaphthenequinone in the presence of olefins

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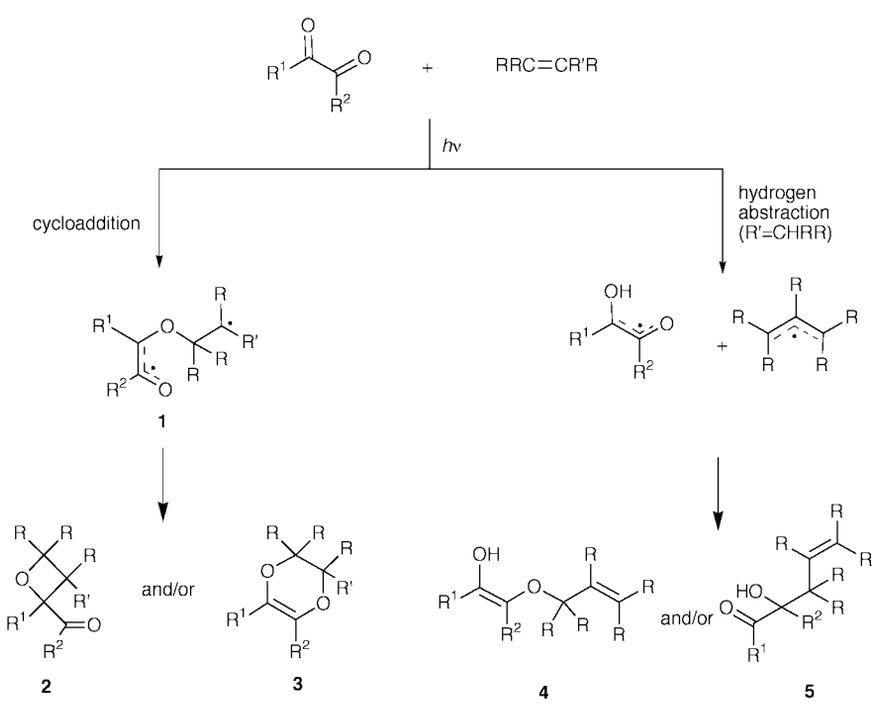
The rate constants for the quenching of acenaphthenequinone triplet by olefins, in degassed benzene solution, have been measured by laser flash photolysis. The alkenes studied included acyclic, cyclic, isolated and conjugated dienes, and vinyl ethers. The quenching rate constant ranges from 2.1×10^6 M^{-1} s^{-1} for hexa-1,5-diene to 6.0×10^8 M^{-1} s^{-1} for 2,3-dimethylbut-2-ene. A plot of log k_q *versus* the ionization potential for some of the olefins employed is linear ($r = 0.89$), with a slope of −1.5/eV. The magnitude of this slope, as well as the inverse solvent effect found in the quenching process, *i.e.* k_q(ACN)/k_q(benzene) = 0.3–0.5, are consistent with a mechanism involving a partial charge transfer complex. Steady state photolysis of acenaphthenequinone in the presence of cyclohexene, 2-methylbut-1-ene, 2-methylbut-2-ene, *trans*-penta-1,3-diene, *cis*-penta-1,3-diene, *trans*-stilbene, *cis*-stilbene, ethyl vinyl ether, and 2,5-dimethylhexa-2,4-diene led only to products resulting from a photocycloaddition process.

Introduction

The photochemical reaction of α-diketones (generally *via* triplet states) with olefins may involve two competing processes:[1] addition to give a biradical (**1**) or abstraction of an allylic hydrogen, when available, to give the semidione/allylic radical pair. Biradical **1** can fragment to starting material or collapse to keto-oxetanes (**2**), the very well known Paternò–Büchi reaction, or to dioxines (**3**). The latter pair may disproportionate back to starting material (or isomerized olefin) or couple to give products **4** or **5** (Scheme 1). Thus, four types of products (often involving stereoisomers) may be formed in dione–olefin reactions. Previous studies indicate that the product composition shows solvent and temperature dependence and that it is rather difficult to make any prediction of results.[1]

The occurrence of an exciplex or radical ion pair prior to biradical formation has frequently been postulated.[2–6] The question arises as to whether the extent of charge transfer in the quenching step involves full electron transfer, resulting in the formation of a radical ion pair, or only leads to a polarized charge transfer complex. The kinetics of quenching by electron transfer can be quantitatively related to thermodynamic properties of triplet carbonyl–electron donor complexes.[2–6] The use of the more readily available ionization potentials of the donors instead of their oxidation potentials slightly changes the Rehm–Weller equation for electron-transfer processes.[7] Therefore, the operating mechanism can also be described in terms of the reduction potential of the nπ* state of the excited triplet ketone and the ionization potential of the olefin.

The most extensively studied diketone has been biacetyl.[1] A



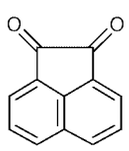
Scheme 1

detailed mechanistic study of its reaction with a number of olefins has appeared.[8] Biacetyl undergoes oxetane formation with ethenes and the regioselectivity is generally higher than that observed in the corresponding reactions of monoketones. It was suggested that a triplet exciplex is the precursor of the 1,4-biradical.[8–11] The strong charge-transfer character of these exciplexes, or even the involvement of contact ion-pair and/or dipolar intermediates, is supported by an extensive study of the reaction of biacetyl with strong electron-donating olefins.[12]

The interaction of *ortho*-quinones with olefins occurs by the formation of a biradical that can lead to [4 + 2] and/or [2 + 2] cyclization products and/or regenerates the quinone with consequent olefin isomerization. The keto-oxetane is photochemically unstable and is either converted back into reagents or into a dioxole.[13–15] With the *ortho*-quinones naphtho-1,2-quinone,[16–18] tetrachloro-*ortho*-benzoquinone[19,20] and 9,10-phenanthrenequinone[21] this reaction preferentially results in the formation of the [4 + 2] photocyclization product, although in some cases keto-oxetanes are obtained as the main product.[22–24] On the other hand, it was shown recently that the reaction of acenaphthenequinone with *trans,trans*-1,4-diphenylbuta-1,3-diene gives only the corresponding keto-oxetane.[25]

The photoreaction of phenanthrene-9,10-quinone with olefins bearing allylic hydrogens shows that cyclization and hydrogen abstraction reactions are competitive. The yield of the hydrogen abstraction product increases when the number of substituents on the olefins increases, indicating that steric hindrance reduces the likelihood of formation of cyclization products.[26]

This paper will present the results of steady state and laser flash photolysis of **6** with several olefins.



6

Results and discussion

Laser flash photolysis

The triplet state of **6** has recently been characterized by laser flash photolysis by our group and shows strong absorptions at 570 and 610 nm, with a lifetime around 1.5 μs in acetonitrile solution.[27] The diketone **6** has a triplet energy of 52 kcal mol^{-1},[28,29] with its lowest triplet state having nπ* character.[30,31]

Rate constants for the quenching of acenaphthenequinone triplet by olefins were measured by laser flash photolysis. Addition of olefins led to a shortening of the triplet lifetime of **6**. The decay of this triplet, monitored at 610 nm, followed pseudo-first order kinetics in the presence of olefins. The experimentally observed pseudo-first order kinetic rate constant, k_{obs}, is related to the quenching rate constant, k_q, according to eqn. (1), where k_o is the decay rate constant of the triplet

$$k_{obs} = k_o + k_q[Q] \quad (1)$$

in the absence of quencher, and [Q] the quencher concentration. Plots based on this equation for the triplet of **6** being quenched by various olefins were found to be linear, from which one can determine k_q values. Fig. 1 shows some quenching plots for **6** by various olefins, in benzene, whereas the rate constants obtained from these plots are shown in Table 1. This table also contains some rate constants obtained in acetonitrile solution. It should be noted that these are overall rate constants and may contain contributions from physical quenching in addition to quenching of the triplet by hydrogen abstraction in a radical-like process and/or addition to the double bond.

Table 1 Rate constants for the reactions of acenaphthenequinone triplet with olefins in benzene solution

Olefin	k_q [a]/M^{-1} s^{-1}	log k_q	IP [b]/eV
Cyclohexa-1,4-diene (**7a**)	9.6×10^7	8.0	8.82
	3.2×10^6 [c]		
Hexa-1,5-diene (**7b**)	2.1×10^6		
Cyclohexene (**7c**)	3.1×10^7	7.5	8.95
	1.7×10^7 [c]		
2-Methylbut-1-ene (**7d**)	1.0×10^7	7.0	9.12
	3.5×10^6 [c]		
2,4,4-Trimethylpent-1-ene (**7e**)	5.8×10^6		
trans-β-Methylstyrene (**7f**)	1.6×10^8		
2-Methylbut-2-ene (**7g**)	1.4×10^8	8.1	8.68
	7.7×10^7 [c]		
2,3-Dimethylbut-2-ene (**7h**)	6.1×10^8	8.8	8.27
	2.6×10^8 [c]		
trans-Penta-1,3-diene (**7i**)	1.9×10^8	8.3	8.59
	7.9×10^7 [c]		
Ethyl vinyl ether (**7j**)	3.0×10^8	8.5	8.80
n-Butyl vinyl ether (**7k**)	2.7×10^8		
Isobutyl vinyl ether (**7l**)	2.7×10^8	8.4	8.93
cis-Stilbene (**7m**)	5.3×10^8		
trans-Stilbene (**7n**)	2.3×10^9	9.4	7.70
2,5-Dimethylhexa-2,4-diene (**7o**)	2.4×10^9	9.4	7.91
Cyclohexa-1,3-diene (**7p**)	1.6×10^9	9.2	8.25

[a] Estimated to be accurate to ±10%. [b] Ionization potential from refs. 35, 38, and 39. [c] In acetonitrile solution.

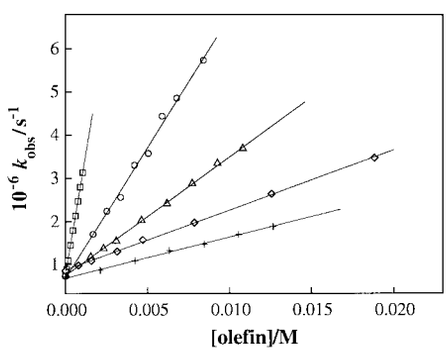


Fig. 1 Quenching plot of the triplet of **6** by several olefins in benzene, λ_{exc} = 355 nm; λ_{mon} = 610 nm. (□) *trans*-Stilbene; (○) 2,3-dimethylbut-2-ene; (Δ) *n*-butyl vinyl ether; (◇) 2-methylbut-2-ene; (+) cyclohexa-1,4-diene.

The transient absorption spectrum recorded after laser photolysis of **6**, at an olefin concentration where all the triplet signal disappeared, does not show any new transient between 200 and 700 nm, an exception being when cyclohexa-1,4-diene was employed. In this case a very weak signal with a maximum at 450 nm was observed and can be attributed to the diketone derived ketyl radical.[27] This is in accord with the very well known fact that cyclohexa-1,4-diene quenches aromatic carbonyl triplets quite efficiently through a hydrogen abstraction reaction.[32]

Assuming that the electron-deficient oxygen of the nπ* acenaphthenequinone triplet would add to the olefin in a radical fashion, then the k_q values we have measured should parallel rate constants for the addition of alkoxy radicals to olefins.[32] This is not the case, since the observed rate constants for the reaction of the triplet of **6** with the alkenes **7a**–**p** are faster (10^6–10^9 M^{-1} s^{-1}) than those predicted for simple radical additions.

It is well known that 1,2-disubstitution on olefins markedly reduces their reactivity towards radical addition.[33] A comparison of the quenching rate constants for 2-methylbut-1-ene, 2-methylbut-2-ene and 2,3-dimethylbut-2-ene indicates an enhancement of these rate constants, and not a decrease, by increasing methyl substitution. This is clear evidence that in this

Table 2 Product distribution for the reaction of the triplet of **6** with several olefins in benzene

Olefin	Product					
	8	%	**9**	%	**10**	%
Cyclohexene (**7c**)	$R^1 = R^3 = H$; $R^2 = R^4 = CH_2(CH_2)_2CH_2$	100				
2-Methylbut-1-ene (**7d**)	$R^1 = R^2 = H$; $R^3 = CH_3$; $R^4 = CH_2CH_3$	47	$R^1 = R^2 = H$; $R^3 = CH_3$; $R^4 = CH_2CH_3$	29	$R^1 = R^2 = H$; $R^3 = CH_3$; $R^4 = CH_2CH_3$	24
2-Methylbut-2-ene (**7g**)	$R^1 = H$; $R^2 = R^3 = R^4 = CH_3$	29			$R^1 = H$; $R^2 = R^3 = R^4 = CH_3$	71
trans-Penta-1,3-diene (**7i**)	$R^1 = R^3 = H$; $R^2 = CH_3$; $R^4 = CH{=}CH_2$	45	$R^1 = R^3 = R^4 = H$; $R^2 = CH{=}CHCH_3$	55		
Ethyl vinyl ether (**7j**)	$R^1 = R^2 = R^3 = H$; $R^4 = OCH_2CH_3$	90			$R^1 = R^2 = R^3 = H$; $R^4 = OCH_2CH_3$	10
cis-Stilbene (**7m**)	$R^1 = R^3 = H$; $R^2 = R^4 = C_6H_5$	100				
trans-Stilbene (**7n**)	$R^1 = R^3 = H$; $R^2 = R^4 = C_6H_5$	100				
2,5-Dimethylhexa-2,4-diene (**7o**)	$R^1 = R^2 = CH_3$; $R^3 = H$; $R^4 = CH{=}C(CH_3)_2$	100				

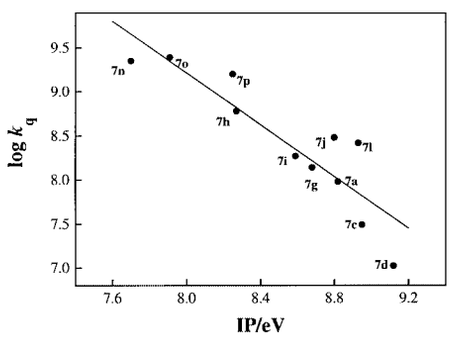


Fig. 2 Dependence of quenching rate constants for the triplet of **6** on olefin ionization potential. Data are shown in Table 1.

case electronic effects predominate over steric effects. These results are in agreement with a mechanism in which alkene quenching of the triplet excited state of **6** involves the formation of a charge-transfer complex, which can collapse to a 1,4-biradical.

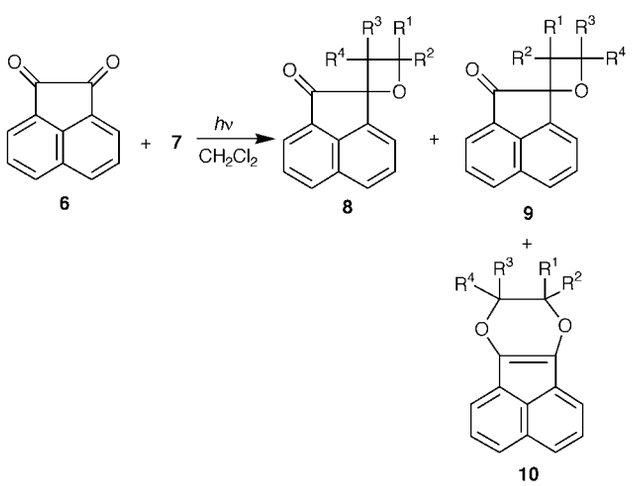
Fig. 2 demonstrates the observed correlation between the k_q values from Table 1 and the ionization potentials of cyclohexa-1,4-diene, cyclohexene, 2-methylbut-1-ene, 2-methylbut-2-ene, 2,3-dimethylbut-2-ene, *trans*-penta-1,3-diene, ethyl vinyl ether, isobutyl vinyl ether, *trans*-stilbene, 2,5-dimethylhexa-2,4-diene and cyclohexa-1,3-diene. Despite its poor correlation coefficient ($r = 0.89$), the plot is reasonably linear with a slope of -1.5/eV. A similar value was previously observed for the quenching of the n,π* triplet of other ketones, such as benzophenone and biacetyl, by olefins.[34] A quenching process which involves essentially a full electron transfer displays a linear log k_q *versus* IP with slope approaching -17/eV, whereas processes involving only partial electron transfer show shallower slopes.[33] The magnitude of the slope of the line in Fig. 2 indicates a small total percent charge transfer in the quenching step, which is in agreement with a mechanism involving a partial charge transfer complex. In this case solvent polarity effects on k_q are not expected. Whereas k_q(ACN)/k_q(benzene) = 13 for full electron transfer,[33] we have found an inverse solvent effect, *i.e.* k_q(ACN)/k_q(benzene) = 0.3–0.5 (ACN = acetonitrile). Small and inverse solvent effects have been observed in many systems believed to involve only fractional charge transfer in the quenching process.[34]

The higher quenching rates for *trans*-stilbene ($E_T = 49.2$ kcal mol^{-1}),[35] 2,5-dimethylhexa-2,4-diene ($E_T = 53.1$ kcal mol^{-1})[36] and cyclohexa-1,3-diene ($E_T = 52.4$ kcal mol^{-1})[35] are consistent with a contribution of the energy transfer process to the triplet quenching, given the relatively low lying triplet level of these quenchers. The lower value for k_q than diffusion control for the last two quenchers can be attributed to the endothermicity of the quenching process due to the low triplet energy of **6**, *i.e.* $E_T = 52$ kcal mol^{-1}.[28,29]

Steady state photolysis

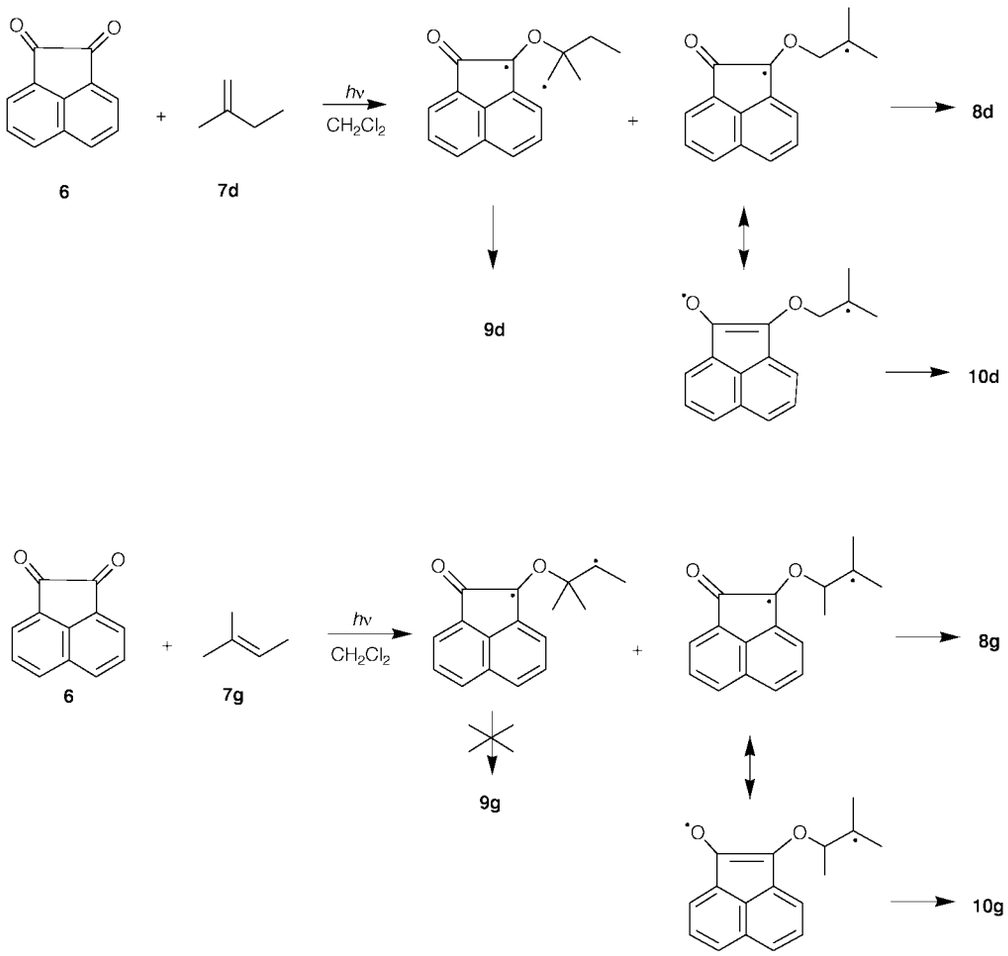
Scheme 2 shows the structure of the products obtained after photolysis of **6** with cyclohexene (**7c**), 2-methylbut-1-ene (**7d**), 2-methylbut-2-ene (**7g**), *trans*-penta-1,3-diene (**7i**), ethyl vinyl ether (**7j**), *cis*-stilbene (**7m**), *trans*-stilbene (**7n**), and 2,5-dimethylhexa-2,4-diene (**7o**).

Analysis of Scheme 2 shows that photolysis of **6** in the presence of the above olefins results only in [2 + 2] and/or [4 + 2] photocycloaddition products (Table 2). Products derived from an initial hydrogen abstraction process were not observed, even when the olefin has allylic hydrogens, as for the case of **7c**,**d**,**g**,**i**,**o**. With the exception of 2-methylbut-2-ene, [2 + 2] photocycloaddition products predominate and, for some of the olefins employed (see Table 2), are exclusively formed. This is in agreement with the recently reported photolysis of acenaphthenequinone and 1,4-diphenylbuta-1,3-diene, in which the only observed product is the corresponding oxetane.[25]



Scheme 2

Even though rate constants for the reaction of the triplet of **6** with olefins are controlled by electronic factors (see above), product distribution seems to be controlled by both electronic and steric effects. The latter influence the distribution of photocycloaddition products, mainly by controlling the approach of the olefin to the carbonyl group. In addition, steric and electronic factors seem to play a significant role in the stabilization of the initially formed 1,4-biradical. Scheme 3 shows a mechanistic proposal for the photocycloaddition of **6** to 2-



Scheme 3

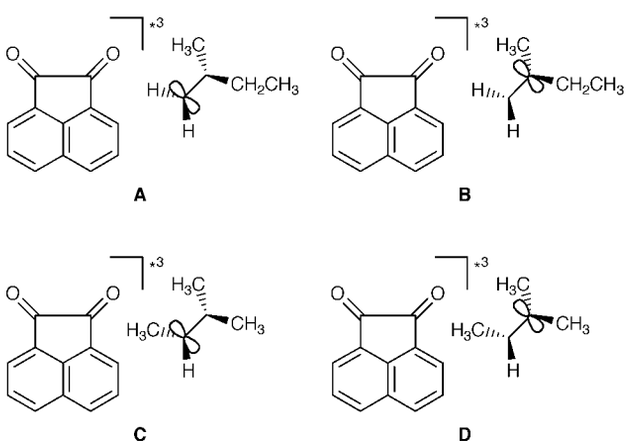


Fig. 3 Possible perpendicular approach between the triplet of **6** and (a) 2-methylbut-1-ene (**7d**) to form **8d** (**A**) and **9d** (**B**), (b) 2-methylbut-2-ene (**7g**) to form **8g** (**C**) and **9g** (**D**). Only the olefin p orbital responsible for the O–C bond formation is indicated.

methylbut-1-ene (**7d**) and 2-methylbut-2-ene (**7g**), in which the influence of these factors is demonstrated.

The formation of the 1,4-biradical precursor of photocycloaddition products in the Paternò–Büchi reaction is commonly described by a symmetry allowed perpendicular approach to a carbonyl double bond. Assuming that this type of approach is involved in the reaction of the triplet of **6** with 2-methylbut-1-ene (**7d**), a small steric effect is expected in the formation of the 1,4-biradical responsible for the formation of either **8d** (Fig. 3A) or **9d** (Fig. 3B). In this case, stabilization of the corresponding 1,4-biradical by an inductive effect due to the presence of alkyl substituents on the carbon-centered radical will be responsible for the observed product distribution. Thus, the most stable 1,4-biradical, having the radical center located on a tertiary carbon, leads to the formation of **8d** (and probably **10d**) in higher yield than **9d**, which is derived from a 1,4-biradical having the radical center on a primary carbon.

Unlike the previous case, the observed product distribution in the photolysis of **6** and 2-methylbut-2-ene (**7g**) can be explained by assuming that steric effects are playing a very important role in the approach of the excited ketone to the olefin (Fig. 3C and 3D). Little steric hindrance is expected for the attack of the electrophilic oxygen of the triplet carbonyl on the p orbital located on carbon-3 of **7g**, which results in the formation of the 1,4-biradical precursor of **8g** (Fig. 3C). On the other hand, the absence of product **9g** can be fully explained by assuming the existence of a strong steric effect in the attack of the excited ketone on carbon-2 of 2-methylbut-2-ene (Fig. 3D).

The predominance of **10g** (71%), in comparison to **8g** (29%), can be explained by the greater stability of the 1,6-biradical precursor of **10g** when compared to that of the corresponding 1,4-biradical. This is a consequence of steric effects associated with the formation of a highly substituted oxetane ring. Results from the literature show that the photolysis of **6** with 2,3-dimethylbut-2-ene leads only to the formation of the [4 + 2] photocycloaddition product.[37] This indicates that the product distribution is affected by steric effects not only on the approach of the reactants but also on the cyclization step leading to the biradical. In this case, biradical cyclization to form a [2 + 2] product through a 1,4-biradical is expected to have a severe steric hindrance when compared to the cyclization leading to the formation of the [4 + 2] product. Using a similar reasoning, one could explain the predominance of **10g** during the photolysis of **6** in the presence of 2-methylbut-2-ene

(Table 2). Similar results were obtained when phenanthrene-9,10-quinone was photolysed in the presence of olefins.[26]

In conclusion, this study shows that rate constants of quenching triplet acenaphthenequinone by olefins are controlled by electronic effects, as determined by laser flash photolysis studies. The value of the slope for the plot log k_q *versus* olefin ionization potential, *ca.* −1.5/eV, reveals that a mechanism involving a partial charge transfer complex must be involved in the quenching process. The irradiation of **6** in the presence of several olefins leads only to products resulting from [2 + 2] and/or [4 + 2] photocycloaddition. Product distribution seems to be controlled by both electronic and steric effects, not only by influencing the approach of the olefin to the carbonyl group, but also by stabilizing the initially formed 1,4-biradical.

Experimental

Materials

The solvents dichloromethane, *n*-hexane, acetone, benzene and acetonitrile, all UV-grade from Aldrich, were used as received. The olefins (from Aldrich) cyclohexa-1,4-diene, hexa-1,5-diene, cyclohexene, 2-methylbut-1-ene, 2,4,4-trimethylpent-1-ene, *trans*-*β*-methylstyrene, 2-methylbut-2-ene, 2,3-dimethylbut-2-ene, *trans*-penta-1,3-diene, ethyl vinyl ether, *n*-butyl vinyl ether, isobutyl vinyl ether, *cis*-stilbene, *trans*-stilbene, 2,5-dimethylhexa-2,4-diene and cyclohexa-1,3-diene were purified when necessary (purity <99%). Acenaphthenequinone (**6**) (Aldrich) was recrystallized from acetic acid.

General techniques

GC-MS analyses were performed on a HP 5987A instrument with a SE-54 capillary column, and GC analysis on a HP 5890 with a RTX-5 capillary column. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 200 spectrometer (^{1}H: 200 MHz; ^{13}C: 50.3 MHz) in $CDCl_3$ using tetramethylsilane (TMS) as the internal standard; *J* values are given in Hz.

All samples were photolysed in a Rayonet reactor equipped with 16 RPR-3500 lamps, at room temperature.

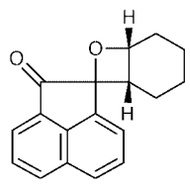
Laser flash photolysis

Laser flash photolysis (LFP) experiments were carried out on an Edinburgh Analytical Instruments LP900 apparatus. Samples were contained in a 10 × 10 mm cell made from Suprasil quartz tubing and deaerated by bubbling with oxygen-free nitrogen for 20 min. The samples were irradiated with a Nd/YAG Surelite laser, using the third harmonic (λ = 355 nm, ≈5 ns, 40 mJ per pulse). The concentration of acenaphthenequinone was chosen in order to give an absorption at the wavelength of excitation (355 nm) of ≈0.6 (concentration ≈0.7 mM). Stock solutions of quenchers in the same solvent employed in sample preparation were prepared so that it was only necessary to add microliter volumes to the sample cell in order to obtain appropriate concentrations of the quencher. All experiments were carried out using benzene or acetonitrile as solvent.

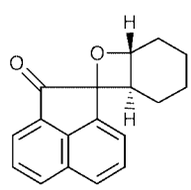
Product studies

Solutions of **6** (300 mg, 1.65 mmol) with various olefins (2–10 mmol) were prepared in dichloromethane (50 ml). The olefins used were cyclohexene (7.0 mmol), 2-methylbut-1-ene (24.5 mmol), 2-methylbut-2-ene (9.5 mmol), *trans*-penta-1,3-diene (10.0 mmol), ethyl vinyl ether (8.5 mmol), *cis*-stilbene (1.5 mmol), *trans*-stilbene (2.5 mmol), and 2,5-dimethylhexa-2,4-diene (2.0 mmol). Samples were contained in quartz tubes and deaerated by bubbling with argon for 30 min, with magnetic stirring at 5 °C. The samples were irradiated until all diketone disappeared (10–85 h), with the reaction being followed by thin-layer chromatography (silica gel; eluent: *n*-hexane–acetone 2:1). After irradiation, the solvent and remaining olefin were removed in a rotary evaporator, under reduced pressure. The residue was purified by preparative thin-layer chromatography using *n*-hexane–acetone 2:1 as eluent and the products identified by ^{1}H and ^{13}C NMR and GC-MS. Products **8** and **9** were complex diastereoisomeric mixtures. Therefore, the structural determination was accomplished using the crude mixture and employing 2-D NMR experiments [Homo- and Hetero-nuclear Correlation Spectroscopy (HOMOCOSY and HETCOSY), $^nJ_{CH}$ (n = 1, 2 or 3)].

8c. ^{1}H NMR (200 MHz, $CDCl_3$, TMS): δ_H 8.11–8.07 (1 H, m, Ph); 7.96–7.88 (4 H, m, Ph); 7.73–7.67 (1 H, m, Ph); 5.64–5.61 (1 H, m, CH); 3.22–3.18 (1H, m, *J* 8.6, CH); 2.08–1.23 (8 H, m, CH_2). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ_C 205.20 (C=O); 141.43; 135.16; 131.59; 130.34; 130.21; 128.06; 125.78; 123.39; 121.53; 89.49; 76.52; 39.92; 28.48; 20.64; 18.88. ^{1}H NMR spectrum in fact corresponds to a mixture of *cis*-**8c** and *trans*-**8c**, which



cis-**8c**



trans-**8c**

could not be resolved by our equipment. MS (*m*/*z*, rel. int.(%)): 264 ($M^{+\bullet}$, 37); 246 (23); 236 (23); 235 (46); 219 (43); 218 (23); 207 (100); 205 (37); 181 (65); 180 (57); 179 (58); 167 (70); 165 (89); 152 (46); 139 (24).

8d. *R*,*S* and *S*,*R*. ^{1}H NMR (200 MHz, $CDCl_3$, TMS): δ_H 8.05–8.01 (2 H, m, Ph); 7.86–7.82 (2 H, m, Ph); 7.68–7.65 (2 H, m, Ph); 4.93 (1 H, d, *J* 9.8, CH_2); 4.38 (1 H, d, *J* 9.8, CH_2); 1.97–1.70 (2 H, m, CH_2); 1.32 (3 H, s, Me); 0.44 (3 H, m, CH_3). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ_C 203.71 (C=O); 141.25; 141.21; 131.41; 130.19; 128.16; 125.55; 122.97; 120.94; 120.87; 94.60; 81.18; 48.59; 27.78; 21.64; 7.84.

R,*R* and *S*,*S*. ^{1}H NMR (200 MHz, $CDCl_3$, TMS): δ_H 8.05–8.01 (2 H, m, Ph); 7.86–7.82 (2 H, m, Ph); 7.68–7.65 (2 H, m, Ph); 4.80 (1 H, d, *J* 10.0, CH_2); 4.48 (1 H, d, *J* 10.0, CH_2); 1.97–1.70 (2 H, m, CH_2); 1.21 (3 H, s, Me); 0.47 (3 H, m, Me). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ_C 203.71 (C=O); 141.25; 141.21; 131.41; 130.19; 128.16; 125.55; 122.97; 120.94; 120.87; 94.40; 80.42; 47.74; 30.06; 18.24; 8.64. MS (*m*/*z*, rel. int.(%)): 252 ($M^{+\bullet}$, 3); 223 (80); 222 (100); 207 (76); 195 (30); 182 (36); 179 (47); 165 (36); 154 (70); 126 (38).

8g. ^{1}H NMR (200 MHz, $CDCl_3$, TMS): δ_H 8.09–8.05 (1 H, m, Ph); 7.91–7.84 (2 H, m, Ph); 7.77–7.63 (3 H, m, Ph); 5.30 (1 H, q, *J* 6.2, CH); 1.43 (3 H, d, *J* 6.2, Me); 1.14 (6 H, s, Me). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ_C 131.29; 131.21; 127.90; 125.27; 124.98; 120.77; 86.13; 84.36; 46.43; 22.48; 19.63; 16.71. MS (*m*/*z*, rel. int.(%)): 252 ($M^{+\bullet}$, absent); 237 (32); 208 (27); 184 (45); 183 (32); 182 (45); 154 (100); 126 (40); 70 (30); 55 (21).

trans-**8i**. ^{1}H NMR (200 MHz, $CDCl_3$, TMS): δ_H 7.52–7.49 (1 H, m, Ph); 7.44–7.33 (3 H, m, Ph); 7.24–7.09 (2 H, m, Ph); 5.73-5.59 (1 H, m, C*H*=CH_2); 4.95–4.83 (1 H, m, CHO); 4.48–4.36 (2 H, m, CH_2); 3.20–3.12 (1 H, m, C*H*CH=CH_2); 1.17 (3 H, d, *J* 5.9, Me). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ_C 202.10 (C=O); 140.40; 137.47; 132.82; 131.90; 130.77; 129.89; 127.94; 125.02; 120.50; 119.81; 118.15; 87.21; 78.99; 56.78; 22.11.

cis-**8i**. ^{1}H NMR (200 MHz, $CDCl_3$, TMS): δ_H 7.52–7.49 (1 H, m, Ph); 7.44–7.33 (3 H, m, Ph); 7.24–7.09 (2 H, m, Ph); 5.73–5.59 (1 H, m, C*H*=CH_2); 4.82–4.71 (1 H, m, CHO); 4.48–4.35 (2 H, m, CH_2); 3.19–3.12 (1 H, m, C*H*CH=CH_2); 1.29 (3 H, d, *J* 5.9, Me). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ_C 202.10 (C=O); 140.40; 137.47; 132.82; 131.90; 131.00; 130.77; 129.89; 127.94; 125.02; 120.50; 119.81; 117.44; 87.21; 78.99; 51.78; 21.54. Percentages for these two diastereoisomers were not determined

since their NMR signals are superimposed. However, from some of the ^{1}H and ^{13}C NMR signals it is possible to observe that the *trans* isomer is in higher percentage than *cis*. MS (*m*/*z*, rel. int.(%)): 250 ($M^{+\bullet}$, absent); 182 (53); 154 (94); 126 (100).

8j. ^{1}H NMR (200 MHz, $CDCl_3$, TMS): δ_H 8.04–7.98 (2 H, m, Ph); 7.88–7.84 (2 H, m, Ph); 7.71–7.63 (2 H, m, Ph); 5.11–5.05 (1 H, m, CH_2); 4.83–4.76 (1 H, m, CH_2); 4.76–4.70 (1 H, m, CH); 3.02–2.96 (1 H, m, MeCH_2); 2.62–2.54 (1 H, m, MeCH_2); 0.75 (3 H, t, *J* 6.9, Me). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ_C 201.82; 141.68; 133.88; 131.89; 130.10; 129.94; 128.46; 127.46; 125.96; 123.66; 121.72; 92.88; 77.00; 75.85; 65.00; 14.44. MS (*m*/*z*, rel. int.(%)): 254 ($M^{+\bullet}$, absent); 224 (68); 196 (80); 195 (100); 181 (40); 167 (19); 139 (75); 72 (83); 44 (33).

8m (8n). *R*,*S* and *S*,*R*. ^{1}H NMR (200 MHz, $CDCl_3$, TMS): δ_H 8.15–7.90 (2 H, m, Ph); 7.83–7.69 (3 H, m, Ph); 7.65–7.60 (2 H, m, Ph); 7.50–7.35 (4 H, m, Ph); 7.15–7.05 (3 H, m, Ph); 6.95–6.92 (1 H, m, CH); 6.84–6.73 (2 H, m, Ph); 5.10 (1 H, d, *J* 8.6 Hz, CH). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ_C 204.46; 202.72; 141.70; 139.31; 138.13; 134.94; 133.56; 131.97; 131.52; 130.25; 130.08; 129.35; 128.40; 128.20; 128.04; 127.60; 127.38; 127.01; 126.83; 126.24; 125.30; 124.32; 121.91; 121.52; 89.77; 88.51; 83.01; 82.16; 81.85; 81.51; 59.87; 53.71.

R,*R* and *S*,*S*. ^{1}H NMR (200 MHz, $CDCl_3$, TMS): δ_H 8.15–7.90 (1 H, m, Ph); 7.83–7.69 (6 H, m, Ph); 7.65–7.60 (2 H, m, Ph); 7.15–7.05 (7 H, m, Ph); 6.84–6.80 (1 H, m, CH); 4.81 (1 H, d, *J* 8.6, CH). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ_C 202.72; 142.30; 138.13; 134.94; 131.99; 131.52; 130.08; 128.84; 128.24; 127.60; 126.83; 126.24; 125.95; 124.32; 124.06; 121.52; 88.51; 81.85; 50.89. MS (*m*/*z*, rel. int.(%)): 362 ($M^{+\bullet}$, absent); 256 (55); 255 (100); 226 (25).

8o. ^{1}H NMR (200 MHz, $CDCl_3$, TMS): δ_H 8.04–8.00 (1 H, m, Ph); 7.91–7.81 (3 H, m, Ph); 7.72–7.64 (2 H, m, Ph); 5.44 (1 H, d, *J* 9.1, CHO); 3.98 (1 H, d, *J* 9.1, C*H*=CMe$_2$); 1.84 (3 H, s, Me); 1.68 (3 H, s, Me); 1.50 (3 H, s, Me); 1.28 (3 H, s, Me). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ_C 203.93; 141.77; 137.21; 136.22; 131.61; 128.81; 128.30; 125.44; 123.03; 121.48; 118.24; 86.37; 85.02; 81.43; 53.21; 48.84; 30.27; 26.09; 25.70; 18.33. MS (*m*/*z*, rel. int.(%)): 292 ($M^{+\bullet}$, absent); 234 (42); 219 (100); 110 (68); 95 (40).

9d. *R*,*S* and *S*,*R*. ^{1}H NMR (200 MHz, $CDCl_3$, TMS): δ_H 8.05–8.01 (2 H, m, Ph); 7.86–7.82 (2 H, m, Ph); 7.68–7.65 (2 H, m, Ph); 2.85–2.64 (2 H, m, CH_2); 2.20–2.10 (2 H, m, CH_2); 1.87 (3 H, br s, Me); 0.99 (3 H, m, Me). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ_C 203.71 (C=O); 141.25; 141.21; 131.41; 130.19; 128.16; 125.55; 122.97; 120.94; 120.87; 82.94; 80.86; 41.00; 36.25; 24.94; 7.84.

R,*R* and *S*,*S*. ^{1}H NMR (200 MHz, $CDCl_3$, TMS): δ_H 8.05–8.01 (1 H, m, Ph); 7.86–7.82 (3 H, m, Ph); 7.68–7.65 (2 H, m, Ph); 2.85–2.64 (2 H, m, CH_2); 1.80–1.70 (2 H, m, CH_2); 1.68 (3 H, br s, Me); 0.47 (3 H, m, Me). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ_C 203.71 (C=O); 141.25; 141.21; 131.41; 130.19; 128.16; 125.55; 122.97; 120.94; 120.87; 82.94; 80.86; 41.00; 33.99; 26.73; 8.68. MS (*m*/*z*, rel. int.(%)): 252 ($M^{+\bullet}$, 2); 223 (80); 182 (64); 180 (5); 154 (100); 126 (27).

9i-*E*. ^{1}H NMR (200 MHz, $CDCl_3$, TMS): δ_H 7.52–7.49 (1 H, m, Ph); 7.44–7.33 (3 H, m, Ph); 7.24–7.09 (2 H, m, Ph); 5.48–5.36 (1 H, m, C*H*=CHMe); 4.95–4.83 (1 H, m,); 4.67–4.60 (1 H, m, CH_2); 4.48–4.36 (1 H, m, CH_2); 3.73–3.57 (1H, m, CH=C*H*Me); 1.01 (3 H, d, *J* 5.84, Me). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ_C 201.66 (C=O); 140.40; 137.61; 132.82; 131.00; 130.77; 129.89; 129.30; 127.94; 125.38; 125.02; 120.50; 119.81; 91.49; 72.91; 48.54; 16.92.

9i-*Z*. ^{1}H NMR (200 MHz, $CDCl_3$, TMS): δ_H 7.52–7.49 (1 H, m, Ph); 7.44–7.33 (3 H, m, Ph); 7.24–7.09 (2 H, m, Ph); 5.20–5.10 (1 H, m, C*H*=CHMe); 4.10–3.90 (1 H, m, CH=C*H*Me); 4.67–4.60 (1 H, m, CH_2); 4.48–4.36 (1 H, m, CH_2); 3.73–3.57 (1 H, m, C*H*CH=CHMe); 1.01 (3 H, d, *J* 5.84, Me). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ_C 201.66 (C=O); 140.40; 137.61; 132.82; 131.00; 130.77; 129.89; 129.30; 127.94; 125.02; 120.50; 119.81; 90.70; 73.01; 44.42; 16.92. Percentages for these two diastereoisomers were not determined since their NMR signals are superimposed. However, from some of the ^{1}H and ^{13}C NMR signals it is possible to observe that the *E* isomer is in higher percentage than *Z*. MS (*m*/*z*, rel. int.(%)): 250 ($M^{+\bullet}$, 28); 235 (22); 221 (31); 220 (31); 205 (68); 182 (34); 154 (100); 126 (54).

10d. ^{1}H NMR (200 MHz, $CDCl_3$, TMS): δ_H 7.60–7.40 (2 H, m, Ph); 7.40–7.35 (4 H, m, Ph); 4.07 (1 H, d, *J* 11.1, CH_2); 3.98 (1 H, d, *J* 11.1, CH_2); 1.89–1.70 (2 H, m, CH_2Me); 1.38 (3 H, s, Me); 1.03 (3 H, t, *J* 7.4, Me). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ_C 136.31; 135.18; 131.70; 131.34; 127.27; 127.00; 126.15; 125.75; 118.64; 118.22; 76.79; 72.42; 28.39; 20.00; 7.69. MS (*m*/*z*, rel. int.(%)): 252 ($M^{+\bullet}$, 22); 183 (31); 182 (34); 154 (100); 126 (28).

10g. ^{1}H NMR (200 MHz, $CDCl_3$, TMS): δ_H 7.60–7.40 (2 H, m, Ph); 7.40–7.30 (4 H, m, Ph); 4.06 (1 H, q, *J* 6.4, CH); 1.42 (3H, br s, Me); 1.39 (3 H, s, Me); 1.32 (3 H, br s, Me). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ_C 135.19; 134.64; 131.05; 130.78; 130.34; 126.54; 126.31; 125.28; 124.97; 117.74; 117.46; 77.30; 76.67; 23.74; 17.90; 15.07. MS (*m*/*z*, rel. int.(%)): 252 ($M^{+\bullet}$, 25); 183 (33); 182 (37); 154 (100); 126 (28).

10j. ^{1}H NMR (200 MHz, $CDCl_3$, TMS): δ_H 8.61 (1 H, d, *J* 7.1, Ph); 8.28 (1 H, d, *J* 7.9, Ph); 8.12 (1 H, d, *J* 7.9, Ph); 7.94 (1 H, d, *J* 6.3, Ph); 7.80–7.72 (2 H, m, Ph); 5.76 (1 H, m, CH); 4.60 (1 H, m, CHCH_2O); 4.30 (1 H, m, *J* 8.2, CHCH_2O); 3.86 (1 H, m, CHCH_2O); 3.63 (1 H, m, OCH_2CH$_3$); 1.31 (3 H, t, *J* 6.9, Me). Due to the very small amount of **10j** it was not possible to get the ^{13}C NMR spectrum. MS (*m*/*z*, rel. int.(%)): 254 ($M^{+\bullet}$, absent); 225 (7); 182 (6); 154 (26); 126 (31); 72 (100); 44 (42); 43 (23).

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