

CONCERNING THE MECHANISM OF INTERACTION OF TRIPLET
BENZOPHENONE WITH NORBORNADIENES AND QUADRICYCLENES

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Norbornadiene (1) and quadricyclene (2) undergo photointerconversion in the presence of certain aromatic-ketone and -aldehyde triplet sensitizers.^{1, 2, 3} The position of the photostationary state thus obtained depends on the triplet energy of the donor. This has been interpreted in terms of a non-spectroscopic excitation of 2 to either the Franck-Condon triplet of 1 or an intermediate biradical; the different internal energies of 1 and 2 could thus account for the importance of the donor triplet energy on the position of the photostationary state.^{1, 2} It has recently been shown that with benzophenone triplet this system decays to give 1:1 adducts,* principally 3 and 4 in high chemical yield,^{5, 6} and we have presented kinetic evidence which shows that the adducts are formed by addition of benzophenone triplet to quadricyclene (2) rather than norbornadiene (1).⁶ We report here an investigation of the reactivities of the ethoxycarbonyl derivatives 5 and 6 towards benzophenone triplet and a comparison of these reactivities with those of 1 and 2 and related systems.

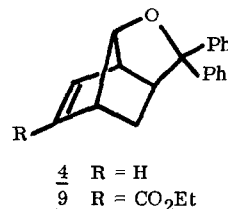
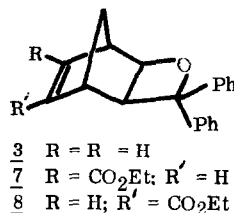
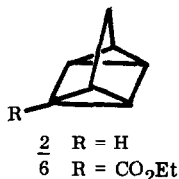
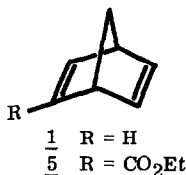
Irradiation of a benzene solution of 5 (0.004M) and benzophenone (0.046M) at 313 nm** resulted in complete decay of starting material with zero-order kinetics (Fig 1). The rate of production of the single product (6)*** corresponded to the decay of 5 up to 80% conversion.

In contrast, irradiation (pyrex) of a benzene solution of 6 (0.004M) and benzophenone (0.046M) resulted in decay of 6 via first-order kinetics (Fig 2) to give 7, 8 and 9 in the ratio 4.5:1:1. Their structures follow from comparison of spectral data with those of 3 and 4.

*Acetophenone gives analogous products in high yield.⁴

**Potassium chromate (0.002M) in 1% aqueous potassium carbonate was employed as filter solution;⁷ benzophenone absorbed all the incident light throughout the reaction.

***Identified by comparison with an authentic specimen produced by direct excitation of 5.⁸



The rate equation for the decay of a photoreactive quencher should be of the form

$$-d[\text{quencher}] = \frac{\text{constant} \times k_q [\text{quencher}]}{k_q [\text{quencher}] + k_{sq} [\text{Ph}_2\text{CO}] + k_d}$$

where k_q is the bimolecular rate constant for

quenching, k_{sq} the self-quenching rate constant of benzophenone triplet by benzophenone,⁹ and k_d the decay rate constant of benzophenone triplet in benzene. The different decay kinetics for 5 and 6 at the same concentration suggest that k_q is significantly greater for 5 than for 6; this has been confirmed (see later). Thus, when a more concentrated benzene solution of 6 (0.1M) and benzophenone (0.14M) was irradiated, a change to zero-order decay of 6 was observed (Fig 2). *

We have measured the rate constants for quenching of benzophenone triplet (k_q)^{**} for the compounds shown in Table 1. The quantum yields of quadricyclene formation (Φ_q) for 1 and 5 and of adduct formation (Φ_a) for 2, 6, 10, 11 and 12 are also shown.^{***} The maximum possible quantum yield for adduct formation, $\Phi_{\text{max}} = \frac{k_q [\text{quencher}]}{k_q [\text{quencher}] + k_{sq} [\text{Ph}_2\text{CO}] + k_d}$, allows calculation of the percentage of

quenchings (α) which lead to adduct ($\alpha = \Phi_a / \Phi_{\text{max}} \cdot 100$). Assuming that a 1,4-biradical lies on the pathway to oxetane, and recognising that fragmentation of biradical to ground state ketone and quencher may be occurring,^{7,13} α represents a minimum value of quenchings which lead to biradical. Quenchings by the quadricyclenes 2 and 6 produce adducts with the same efficiency ($\sim 9\%$) and this is an order of magnitude greater than for the bicyclic olefins 10, 11 and 12.

A number of groups have discussed the relationship between the efficiency of quenching of ketone triplets and the physical properties of the quencher.¹⁴⁻¹⁷ There is no doubt from this work that in

*The quoted value of $1.6 \times 10^5 \text{ l m}^{-1} \text{ s}^{-1}$ for k_{sq} ⁹ indicates that at the concentrations employed, the self-quenching term is less important than k_d .

**A pulse radiolysis technique was employed for this purpose;¹⁰ the average value determined for k_d = $1.7 \times 10^5 \text{ s}^{-1}$ (cf. quoted values¹¹).

***The only significant photoproducts of reaction of benzophenone triplet with 7, 8 and 9 are oxetanes.¹²

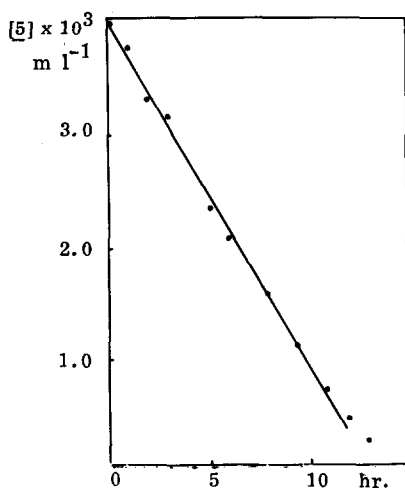


Fig. 1. Decay of 5 (0.004M) to 6.

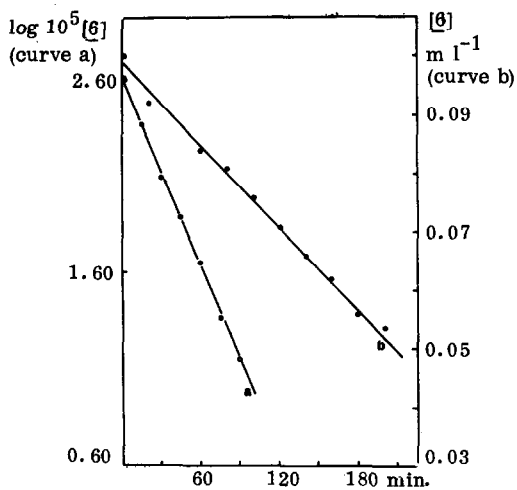


Fig. 2. (a) Decay of 6 (0.004M) to adducts.
(b) Decay of 6 (0.1M) to adducts.

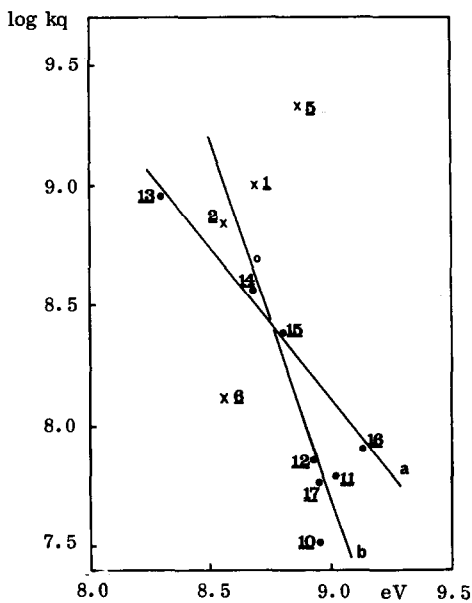
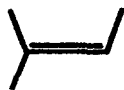


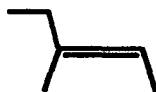
Fig. 3. Log kq for quenching of benzophenone triplet vs ionisation potential of quencher.



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many instances charge-transfer interaction plays an important role in the quenching act. We have restricted ourselves to a comparison of the k_q values and ionisation potentials in Table 1 with those published for olefins and triplet benzophenone.^{14, 15a} The least squares plots shown in Fig 3 have been obtained without inclusion of the compounds of immediate interest to us, i.e. 1, 2, 5 and 6. Olefins 13-16 apparently show a good correlation (line (a)) but, in contrast to an earlier suggestion¹⁴, it appears to us that the gradient will be lowered because 13 is more sterically hindered, 16 less hindered, than are 14 and 15 to complex formation. If one omits 13 and 16, line (b) (Fig 3) is obtained for 10, 11, 12^{*}, 14, 15 and 17 and we feel that this more closely represents the sensitivity of quenching of benzophenone triplet to changes in the electron donating ability of the quencher.

The corresponding points (X) for 1, 2, 5 and 6 are also shown in Fig. 3. A marked contrast is immediately obvious. Introduction of an ester function into 1 to give 5 results in a significant increase in k_q although the electron donating capacity decreases; the ester function causes a decrease in k_q on

Table 1

Quencher	k_q ($1 \text{ m}^{-1} \text{ s}^{-1}$)	Φ_q	Φ_a	α	IP (eV)
norbornadiene (<u>1</u>)	9.7×10^8	$0.54^{\text{b**}}$		-	8.69^{c}
quadricyclene (<u>2</u>)	8.3×10^8	-	0.09^{a}	9.2	8.56^{d}
ethoxycarbonyl-norbornadiene (<u>5</u>)	2.1×10^9	0.85^{a}	-	-	8.87^{d}
ethoxycarbonyl-quadricyclene (<u>6</u>)	1.3×10^8	-	0.08^{a}	9.1	8.56^{d}
norborn-2-ene (<u>10</u>)	3.2×10^7	-	0.004^{a}	0.63	8.95^{c}
2-methylenenorbornane (<u>11</u>)	6.2×10^7	-	0.01^{a}	1.3	9.02^{d}
5-methylenenorborn-2-ene (<u>12</u>)	1.4×10^8	-	0.007^{a}	0.79	8.93^{d}
a 0.01M	b 0.1M	c = Ref. 18	d = This work	***	

going from 2 to 6 with no change in the electron donating capacity. **** Quadricyclene (2) clearly lies in a

*The value for k_q has been corrected for the statistical increase due to the presence of 2 double bonds, one of the norbornene type, one of the 2-methylenenorbornane type.

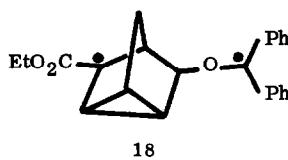
**This compares with the original value of 0.51 obtained in ether solution (0.579M.)³

***Vertical ionisation potentials were very kindly determined from photoelectron spectra by Dr. R.A.W. Johnstone of the University of Liverpool.

****The first ionisation processes of 5 and 6 have essentially the same orbital origin as for 1 and 2 respectively. ¹⁹

position on the graph which is consistent with a normal charge-transfer mechanism. Although the ester function in 6 does not raise the ionisation potential relative to that of 2 it lowers the quenching efficiency presumably due to steric hindrance.

It therefore seems very probable that the benzophenone sensitised conversion of 2 to 1 involves decay of an intermediate charge-transfer complex of 2 and benzophenone triplet to give 1 and benzophenone. This mechanism is known to operate in the corresponding hydrocarbon singlet sensitized process.²⁰ An alternative mode of decay of this complex is to biradicals which give, at least in part, an oxetane and an ether. It is of interest that more than 85% of the adducts from 6 (7 and 9) are formally derived from the biradical 18 which, on radical stability grounds, would be the anticipated product of ketone triplet attack on 6. This result is, however, open to a number of interpretations.



From Fig 3 it is apparent that quenching by the ethoxycarbonylnorbornadiene (5) cannot be the result of charge-transfer interaction. A low triplet energy leads to a rate constant for collisional-transfer which approaches diffusion control. The situation for norbornadiene (1) itself is somewhat ambiguous. The two extreme interpretations of its position well above line (b) (Fig 3) are (a) that a predominantly collisional-transfer mechanism operates and this becomes faster for 5 due to a lower triplet energy, or (b) that a particularly favourable steric requirement for charge-transfer interaction exists in this case. The latter seems unlikely, especially on consideration of the position of norbornene (10) on the sterically unfavourable side of line (b) (Fig 3). However k_q for 1 could possibly be raised by a factor of 2 due to the presence of 2 complexing sites. Correction for this gives a point (O) which is virtually on line (b).

It seems likely that both mechanisms are operating in the case of 1; certainly exclusive collisional-transfer appears to be ruled out for the following reasons. The quantum yield of the acetophenone sensitized conversion of 1 to 2 is 0.96 at 0.1M,^{*} i.e. a minimum of 96% of quenchings by 1 give 2. The values of k_q and k_d for 1 and benzophenone triplet allow a maximum quantum yield of 1.0 for the

^{*}This compares with a value of 0.91 determined in ether solution (0.528M).³

conversion of 1 to 2 at this concentration whereas the experimental value of 0.54 (Table 1) shows that only 54% of quenchings of benzophenone triplet by 1 give 2. Acetophenone has a higher triplet energy (73.6 kcal mole⁻¹) than benzophenone (68.6) and therefore quenching by collisional-transfer should be more favourable for the former. Thus, even if all the quenchings of acetophenone triplet by 1 in benzene proceed via collisional-transfer to give free triplets of 1, \gg 96% of which must collapse to quadricyclene, a maximum of only 56% of quenchings of benzophenone triplet by 1 in benzene can proceed via the same mechanism, 96% of the free triplets of 1 thus formed collapsing to 2 to give a quantum yield of 0.54. A minimum of 44% of quenchings of benzophenone triplet by 1 must therefore proceed via some process other than collisional-transfer. Since Schenck biradicals are apparently not formed⁶ charge-transfer complexation appears to be the only possibility.

The triplet sensitised conversion of 1 to 2 would thus appear to involve either a) decay of an intermediate charge-transfer complex for which the decay ratio to 1 and 2 (and sensitizer) depends on the triplet energy of the electron acceptor in the complex, or b) decay of free triplets of 1 to 2. Both mechanisms combined with that proposed for the triplet sensitised conversion of 2 to 1, would explain the original findings that the position of the photostationary state between 1 and 2 is dependent on the triplet energy of the sensitizer.^{1,2}

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