THE REACTION OF TRIPLET BENZOPHENONE WITH

5-METHYLENENORBORN-2-ENE: REGIOSPECIFIC OXETANE FORMATION

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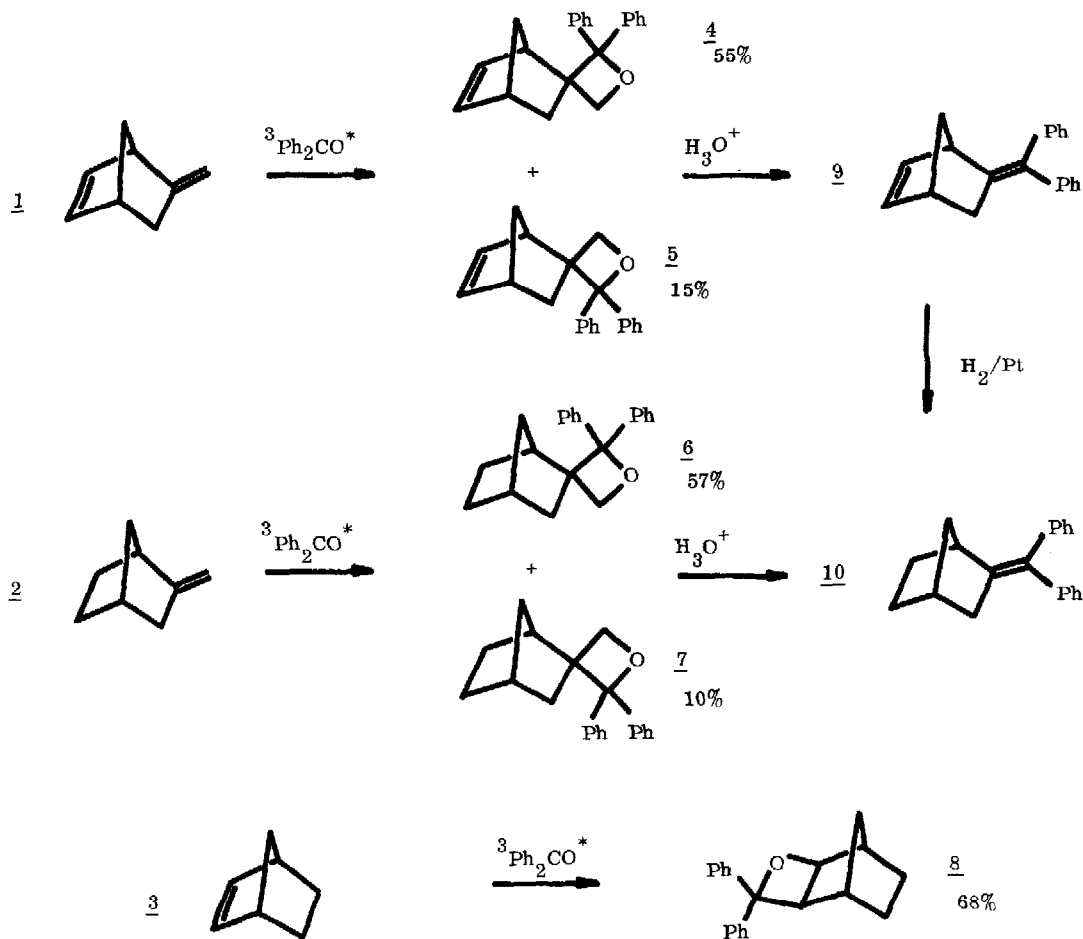Department of Chemistry, The University, Manchester M13 9PL.

Aromatic ketones with low lying n, π^* triplet states undergo light-induced addition to simple olefins

to give oxetanes[1] and generally the major product is the oxetane derived from the most stable biradical.

However, a number of exceptions are in accord with the suggestion that the product geometry is determined

by the interaction of the reactants within a pre-biradical complex, which is now widely considered to be

the primary charge-transfer stabilised product of encounter.[2-4]

We report here an investigation of the light-induced reactions of benzophenone with 5-methylene-

norborn-2-ene (1), 2-methylenenorbornane (2) and norbornene (3). The principal aim of the work was to

determine to what extent homoconjugative interaction between the double bonds of (1) would effect their

relative reactivities with respect to those of the double bonds in (2) and (3).

Deoxygenated benzene solutions of benzophenone (0.015 mol.1^{-1}) containing a 50% excess of olefin were

irradiated in pyrex until the ketone had been consumed. In each case high chemical yields of 1:1 adducts

were produced. These adducts were the oxetanes (4) and (5) from (1), (6) and (7) from (2) and (8) from

(3); they were isolated in the yields shown by dry column chromatography on alumina. The structures

(4) – (7) follow from spectral data, acid catalysed conversion to (9) and (10) and catalytic hydrogenation of

(9) to (10). The reaction to give (8) had previously been described.[5,6] Clearly benzophenone adds

exclusively to the exocyclic double bond of (1).

The rate constants, k_q, for quenching of triplet benzophenone by (1), (2) and (3)[7] and quantum yields

for oxetane formation ϕ_o are shown in Table 1 together with the maximum possible quantum yields for

oxetane formation $\phi_{max} = k_q[\text{olefin}]/k_q[\text{olefin}] + k_{sq}[\text{ketone}] + k_d$, the percentage of quenchings leading

$^3Ph_2CO^*$

H_3O^+

4
55%

1

5
15%

9

H_2/Pt

$^3Ph_2CO^*$

H_3O^+

6
57%

2

7
10%

10

3

$^3Ph_2CO^*$

8
68%

to oxetane, $\alpha = \Phi_o \cdot 100/\Phi_{max}$, and the effective rate constant for production of oxetane $k_o = k_q \Phi_o/\Phi_{max}$.*

As is often the case[3] only a small proportion of quenchings produce oxetane. The data for (2) and (3)

suggest that about 20% of the 1:1 adducts derived from (1) should result from addition to the endocyclic

double bond. No such product is formed even though this should be favoured relative to (3) due to the

increased ring strain in (1).

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* We have used values determined by Singer et al[8] for k_d, the rate constant for decay of triplet benzo-

phenone in benzene $(1.3 \times 10^5 \text{ s.}^{-1})$, and k_{sq}, the self quenching rate constant $(4.4 \times 10^5 \text{ l.mol.}^{-1}\text{s.}^{-1})$.

The use of alternative reported values (cf. ref. 9, 10) does not make a significant difference.

Table 1 Data for the Reaction of Triplet Benzophenone with Olefins

Olefin	k_q/l. mol.$^{-1}$s.$^{-1}$	Φ_0	Φ_{max}	$\alpha/\%$	k_0/l. mol.$^{-1}$s.$^{-1}$
(1)	1.4×10^8	0.007	0.90	0.78	10.9×10^5
(2)	6.2×10^7	0.01	0.80	1.25	7.8×10^5
(3)	3.2×10^7	0.004	0.68	0.59	1.9×10^5

A possible explanation of this result is that homoconjugative interaction between the double bonds of (1) changes the electron availability at the alternative sites of attack. That such interaction occurs is shown by the π-level splitting[11] of 0.33 ± 0.1 eV in (1) compared with (2) and (3) as shown in Table 2. However, the π-ionisation potentials of (2) and (3) are the same within experimental error and they should therefore contribute equally to the highest π-level of (1); i.e. it is not possible to say that one particular double bond is predominantly associated with the lower ionisation potential.[*] In Table 2 are also shown the ^{13}C chemical shifts of the olefinic carbons of (1), (2) and (3). No significant changes are observed for (1) compared with (2) and (3). The electronic properties of the ground state of (1) do not therefore appear to offer an explanation for the total regiospecificity of oxetane formation from this compound and triplet benzophenone.

Table 2 Vertical Ionisation Potentials and ^{13}C Chemical Shifts

Olefin	IP/eV (± 0.05 eV)	^{13}C-double bond resonances	
		endocyclic	exocyclic
(1)	8.93, 9.31	134.4, 136.4	103.3, 149.5
(2)	9.02	–	101.6, 152.4
(3)	8.97	135.4	–

[*] In fact, if the small difference in the measured ionisation potentials of (2) and (3) shown in Table 2 is real, the π-level splitting in (1) should increase complexation at the endocyclic double bond of (1) relative to that at the exocyclic position. This is not in accord with our experiments.

An alternative explanation is that the greater ability of both double bonds in (1) to stabilise a complex by charge-transfer interaction results in an enhanced <u>selectivity</u> with respect to subsequent decay processes. Thus, if two distinct complexes may be formed depending on the double bond involved, it is possible that, with respect to the corresponding mono-olefins, production of an intrinsically less stable biradical from the "endocyclic complex" competes much less favourably with the alternative modes of decay of that complex than does production of a more stable biradical from the "exocyclic complex". The relative α-values in Table 1, which give the percentage of quenchings leading to oxetane, are in agreement with such a situation. The argument that, in our case, biradical formation at an exocyclic double bond is energetically preferred receives limited support from work on free radical additions to (1), (2) and (3). While thiyl radicals add exclusively to the endocyclic double bond of (1)[12] it has been reported that $\cdot CCl_3$ reacts four times faster at the exocyclic double bond.[13] It has been suggested[12] that addition is normally preferred at the endocyclic double bond unless, as in the case of $\cdot CCl_3$, the bulk of the introduced substituent hinders bond formation at this position. The steric requirements of $Ph_2\overset{\bullet}{C}-O-$ may well create a similar situation.

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