Tetrahedron Vol. 36, pp. 397 to 407
Pergamon Press Ltd., 1980. Printed in Great Britain

THE INTER-AND INTRAMOLECULAR ADDITION OF AROMATIC KETONE TRIPLETS TO QUADRICYCLENES

COMPARISON WITH THE CORRESPONDING REACTIVITIES OF NORBORNADIENE, METHYLENENORBORNENE, METHYLENENORBORNANE AND NORBORNENE

A. J. G. Barwise, A. A. Gorman*, R. L. Leyland, C. T. Parekh and P. G. Smith
Chemistry Department, University of Manchester, Manchester M13 9PL, England

(*Received in UK 29 May 1979*)

Abstract—Irradiation of acetophenone or benzophenone in the presence of norbornadiene or quadricyclene gives 1:1-adducts. These arise via reaction of the ketone triplet with the quadricyclene. Similar reactivity is exhibited in an intramolecular sense by 7-phenacylnorbornadiene and the corresponding quadricyclene. Addition of triplet benzophenone to 5-methylene norbornene is regiospecific in contrast to expectations based on a comparison of the reactivities of 2-methylenenorbornane and norbornene. The possibility is raised that, in contrast to the simple olefins and the quadricyclenes, exciplexes formed by reaction of the rigid homoconjugated dienes with the triplet ketone are *endo* orientated with participation of both double bounds.

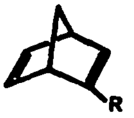
It has been known for many years that the electronically excited states of carbonyl compounds will add to double bonds to form oxetanes. The majority of examples of the Paterno–Büchi reaction,[1,2] as it is known, involve addition of a carbonyl triplet state to a π-system, most commonly an isolated double bond. It is accepted that an intermediate in this reaction is a 1,4-biradical with a lifetime long enough to destroy the stereochemical integrity of an acyclic double bond.[3] Evidence has been put forward to suggest that the biradical is formed via a triplet exciplex or charge-transfer stabilised complex.[4-8] Decay of this exciplex to ground states provides a pathway for energy wastage and the efficiency for adduct formation is normally very low. As far as we are aware definitive data concerning the extent to which biradical formation may be reversible do not exist.

Our interest in such reactions arose from work on the triplet sensitised interconversion of norbornadiene (1) and quadricyclene (2). Hammond *et al.*[9] originally showed that a photostationary state between 1 and 2 is established, the position of which is apparently dependent on the triplet energy of the sensitiser employed. We have since provided evidence that the conversion of 1 to 2 takes place via the free norbornadiene triplet whereas the reverse reaction proceeds via a triplet exciplex.[10] During this work it was noticed that, although irradiation of benzophenone or acetophenone in the presence of norbornadiene (1) or its 2-ethoxycarbonyl analogue (3) led to rapid formation of the corresponding quadricyclenes 2 and 4, loss of volatile material occurred with the formation of 1:1-adducts, apparently derived from the aromatic ketone and the norbornadiene. The results described here show that the adducts arise via addition of the ketone triplet to the corresponding quadricyclene. In connection with these findings we have (a) investigated the intramolecular light-induced reactivity of 7-phenacylnorbornadiene and the two 7-phenacylnorbornenes and (b) compared the reactivity of norbornadiene towards triplet benzophenone with those of 5-methylenenorbornene and the related olefins 2-methylenenorbornane and norbornene. In Table 1 are reproduced triplet quenching rate constants, k_q, triplet self-quenching rate constants, k_{sq}, and rate constants for triplet decay in benzene, k_d, pertinent to this work, which have previously been determined by us.[10]

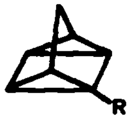
RESULTS

Adducts from irradiation of benzophenone and acetophenone in the presence of norbornadienes and quadricyclenes

Steady state irradiations through pyrex have been performed, using nitrogen purged benzene solutions of either benzophenone or acetophenone in the presence of 1 and 2 or their ethoxycarbonyl analogues 3 and 4. In all cases irradiation in the presence of the norbornadiene led to rapid formation of the corresponding quadricyclene. In the case of benzophenone and 1 a photostationary state, [2]:[1] = 92.5:7.5, was apparently established;[a] in other instances complete conversion to the quadricyclene was observed. For all irradiations loss of volatile material took place to give 1:1-adducts which were isolated by dry column chromatography on alumina. Commencement of the reaction with either the norbornadiene or the corresponding quadricyclene gave the same adducts in essentially the same isolated yields. These data are summarised in Table 2 (experiments 1–8). The chemical yields of isolated adducts are high in the cases of 1 and 2 (80–90%). For 3 and 4 with ben-



1 R = H
3 R = CO_2Et



2 R = H
4 R = CO_2Et

---

[a] A photostationary state, [2]:[1] = 84:16, has been reported for this reaction in ether.[9]

Table 1. Rate constants for reactivity of acetophenone and benzophenone triplets in benzene[a]

Rate Constants	Acetophenone	Benzophenone
(a) $k_q / l\ mol^{-1} s^{-1}$		
norbornadiene (1)	3.9×10^9	9.7×10^8
quadricyclene (2)	4.3×10^8	8.3×10^8
2-ethoxycarbonylnorbornadiene (3)	5.4×10^9	2.1×10^9
2-ethoxycarbonylquadricyclene (4)	6.6×10^8	1.3×10^8
5-methylenenorbornene (26)	-	1.4×10^8
2-methylenenorbornane (27)	-	6.2×10^7
norbornene (28)	1.5×10^8 [b]	3.2×10^7
(b) $k_{sq} / l\ mol^{-1} s^{-1}$	4.6×10^6 [b]	4.0×10^5
(c) k_d / s^{-1}	2.5×10^5	$1:5 \times 10^5$

[a] Reference 10 unless otherwise stated. [b] Reference 11.

zophenone the yields are lower (~50%) and with acetophenone adduct formation is slow and the resulting reaction mixture less clean. This possibly reflects the fact that the quenching of the higher energy triplet by 4 includes a significant energy transfer contribution.[10]

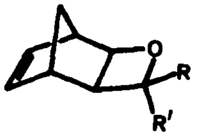
The structures of the adducts follow principally from spectral data (Experimental). In particular the oxetanes showed characteristic strong IR absorption in the 960–970 cm^{-1} region[12] and two one proton doublets ($J = 5$–$6\ Hz$) in their NMR spectra, typical of the two *endo* methine protons, one adjacent to oxygen (5.3 – 5.7 τ). The lack of coupling with the bridgehead hydrogens indicated the *exo* orientation of the oxetane ring. In the case of 5 hydrogenation over platinum gave the known

Table 2. Adducts from irradiation of benzophenone (B) and acetophenone (A) in the presence of norbornadienes, quadricyclenes, methylenenorbornene, methylenenorbornane and norbornene[a]

Experiment	Reactants	Adducts
(1)	B(0.014M), 1 (0.02M)	5 (61%), 6 (26%)
(2)	B (0.014M), 2 (0.02M)	5 (57%), 6 (26%)
(3)	A (0.013M), 1 (0.043M)	7a and 7b (61%), 8a or 8b (18%), unknown (4%)
(4)	A (0.013M), 2 (0.043M)	7a and 7b (57%), 8a or 8b (21%), unknown (4%)
(5)	B (0.0013M), 3 (0.0026M)	as for experiment (6)[b]
(6)	B (0.0013M), 4 (0.0026M)	9 (35%), 10 and 11 (15%)
(7)	A (0.003M), 3 (0.0034M)	two of 12a, 12b, 13a, 13b
(8)	A (0.003M), 4 (0.0034M)	as for experiment (7)[b]
(9)	B (0.011M), 26 (0.021)	29 (55%), 30 (15%)
(10)	B (0.011M), 27 (0.014M)	31 (57%), 32 (10%)
(11)	B (0.062M), 28 (0.096M)	33 (68%)

[a] Irradiation of nitrogen purged solutions through pyrex, 100W medium pressure mercury arc.

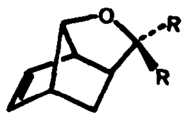
[b] Products only identified by TLC comparison.



5 R = R' = Ph

7a R = Me, R' = Ph

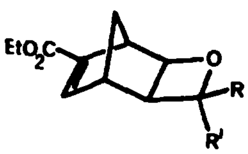
7b R = Ph, R' = Me



6 R = R' = Ph

8a R = Me, R' = Ph

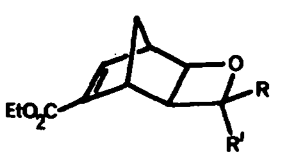
8b R = Ph, R' = Me



9 R = R' = Ph

12a R = Me, R' = Ph

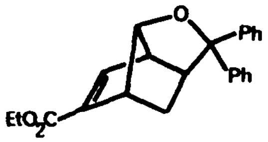
12b R = Ph, R' = Me



10 R = R' = Ph

13a R = Me, R' = Ph

13b R = Ph, R' = Me



11

oxetane formed by addition of triplet benzophenone to norbornene[13,14] (*vide infra*). The 5-ring ethers showed a one proton triplet (5.6 – 5.9 τ; $J \sim 1$ Hz) in their NMR spectra due to the bridge methine proton adjacent to oxygen. The adducts from experiments (7) and (8) could not be properly identified due to difficulties in isolating pure material.

Origin of 1:1-*adducts*. Compounds of types **5** and **6** clearly appear to be products of decay of a set of interconverting biradicals (**14**, **15** and **16**) of the homoallyl⇌cyclopropylcarbinyl type. The identical nature of the final products on reaction of either the norbornadiene or the corresponding quadricyclene suggests that either (a) adducts are formed from only one of these substrates or (b) equilibration of the biradicals, e.g. **14**, **15** and **16**, is fast relative to collapse to products. We have shown that adducts are only formed by addition to the quadricyclenes.

The most clear cut experiments concern the esters **3** and **4** since their relative rates of reaction with the ketone triplets, particularly in the case of benzophenone (see Table 1), allowed better time resolution of the product forming events. On irradiation of benzene solutions of either acetophenone or benzophenone containing **3** under conditions where the ketone absorbed all the incident light (313 nm[15]) throughout the reaction and **3** quenched all the ketone triplets produced, i.e. $k_q[3] > > k_d + k_{sq}$ [ketone] (see Table 1), anticipated zero-order decay of **3** took place. The formation of **4** mirror imaged the decay of **3** up to 70% conversion and thereafter loss of ketone and **4** to give adducts took place (see Fig. 1). Similar experiments with **4** gave slower but zero-order decay to adducts up to > 50% conversion. There is no doubt therefore that in the case of **3** and **4** adducts only arise via **4**.

The situation was more complicated for **1** and **2**, in particular because of the similarity of their rate constants for quenching of triplet benzophenone (Table 1). In an attempt to chronologically differentiate between the reactions of **1** and **2** with the triplet states of acetophenone and benzophenone these ketones were irradiated in neat degassed norbornadiene, the ketone absorbing all the incident light. Initially, in both cases, zero-order production of **2** and no loss of sensitiser were observed (see Fig 2). The subsequent change in the rate of production of **2** and concomitant commencement of decay of sensitiser indicate that, within experimental error, adducts are derived solely from the quadricyclene.[b] [c]

Light-induced reactivity of 7-phenacylnorbornadiene and 7-phenacylnorbornenes

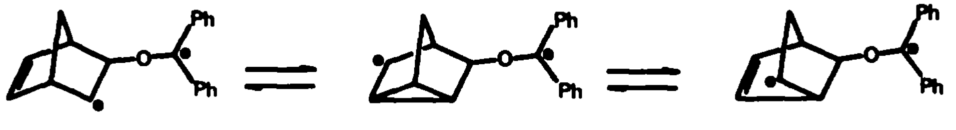
The above results indicate that on irradiation of acetophenone or benzophenone in the presence of norbornadienes **1** and **3** adduct formation only takes place via the corresponding quadricyclenes **2** and **4**. The evidence is however slightly unsatisfactory in the case of norbornadiene due to the use of a neat solution of this reactant. To circumvent this problem we have investigated the photochemistry of 7-phenacylnorbornadiene (**17**), a model for the intramolecular interaction of an acetophenone-like triplet with the norbornadiene system. For comparative purposes we have also investigated the photochemistry of the *syn*-and *anti*-7-phenacylnorbornenes **18** and **19**. These compounds were synthesised via routes described in the experimental section. The UV spectral data for **17**, **18**, **19** and acetophenone are shown in Table 3. These data together with time-resolved

---

[b] Our preliminary communication of this result for benzophenone[16] was preceded by a paper by Kubota *et al.*[17] in which it was claimed that adducts were formed by addition to norbornadiene. Quadricyclene was not mentioned.

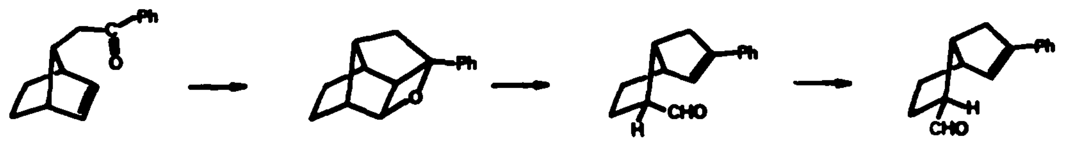
[c] It would appear from Fig. 2 that ~ 20 mM quadricyclene competes effectively with 10.9 M norbornadiene for triplet benzophenone.[d] This would seem to be impossible since the quenching rate constants, admittedly determined in benzene (Table 1), are very similar. A probable explanation is that quenching of triplet norbornadiene by norbornadiene itself is important in neat solution. The effect of such a process would be to slow down quadricyclene formation making addition of ketone triplet to this species competitive at lower than expected concentrations.

[d] In the corresponding experiment decay of acetophenone becomes significant at ~ 70 mM quadricyclene.

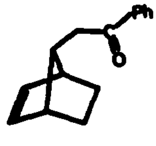


14 15 16

17 20 21 + 22



18 23 24 25



19

experiments[18] and the results to be described indicate that 17, 18 and 19 all have lowest n, π^* triplet states.

Irradiation of nitrogen purged benzene solutions of 17, 18 and 19 through pyrex resulted in rapid loss of ketone within 2 hr in the cases of 17 and 18. After this time 19 remained virtually unchanged. The sole product from 18 was the oxetane 23 whose structure follows from spectral data (Experimental), in particular a strong IR oxetane absorption at $985\ cm^{-1}$ and a one proton NMR doublet ($J = 5$ *Hz*) at 5.88 τ, and its essentially quantitative thermal conversion to the aldehyde 24. The latter isomerises of silica gel to the more stable epimer 25[*]. The final product from 17 contained two components, only one of which, the crystalline cyclobutane derivative 22, has been isolated (~50%) in a homogenous state. In contrast to 23 it was stable towards heat and acid and its structure followed principally from NMR spectral data ($CDCl_3$ and C_6D_6) and a comparison with those of 8a. The second component, although not isolated, appears to be the oxetane 21 on the basis of a doublet at 5.94 τ($J = 5$ Hz) in the NMR spectrum (C_6D_6) of the final product mixture. The ratio of 21:22 was ~2:3; they are clearly the intramolecular equivalents of the oxetane 7a and the ether 8a formed by addition of triplet acetophenone to quadricylene (2). Analysis of the light-induced reaction of 17 by tlc and glc showed no evidence for intermediates on the way to 21 and 22. However, irradiation of a C_6D_6 solution in a sealed degassed pyrex NMR tube clearly indicated the intermediacy of 7-phenacylquadricylene (20). The NMR spectrum of the photoreaction mixture showed the rapid appearance at 8.60 τ of resonances typical of the quadricylene cyclopropane protons[20] at the expense of the olefinic signals of 17. Resonances characteristic of the 7-phenacyl grouping were retained although slightly shifted. In Fig. 3 the NMR integrals of the olefinic protons of 17, the cyclopropane protons of 20, the olefinic protons of 21 and 22 and the signals of 21 and 22 between 7.50 and 8.30 τ (window in the spectra of 17 and 20) are plotted vs time. The plots clearly indicate that the

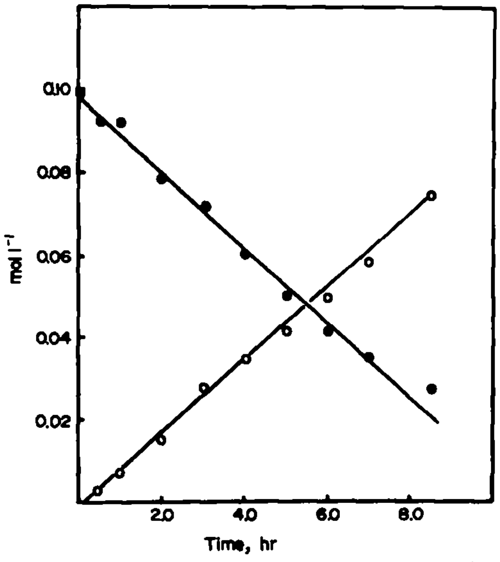


Fig. 1. Irradiation at 313 nm of acetophenone (0.06 mol l^{-1}) and 2-ethoxycarbonylnorbornadiene (3, 0.1 mol l^{-1}) in benzene. Plots of concentrations of 3(●) and 4(○) vs time.

---

[*] The formation of 23 parallels a much earlier result obtained by Sauers *et al.* for *endo*-5-benzoylnorbornene.[19]

Table 3. UV spectral data of phenyl ketones in ethanol

Ketone	λ_{max} (ϵ)
acetophenone	241 (11,970), 278 (1070), 313 (64)
7-phenacylnorbornadiene (17)	243 (16,000), 277 (830), 315 (70)
syn-7-phenacylnorbornene (18)	243 (10,800), 277 (957), 315 (72)
anti-7-phenacylnorbornene (19)	243 (14,230), 282 (1173), 314 (92)

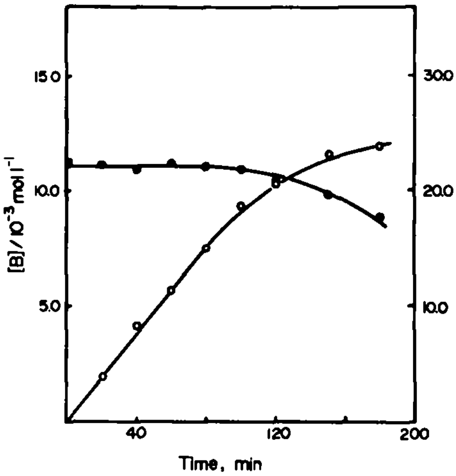


Fig. 2. Irradiation through pyrex of benzophenone (0.011 mol l^{-1}) in norbornadiene. Plots of concentrations of benzophenone (B, ●) and quadricyclene (Q, ○) vs time.

products of intramolecular addition, **21** and **22**, arise *via* the corresponding quadricyclene derivative **20**, a result in agreement with findings concerning the corresponding intermolecular reaction.[f]

Adducts from irradiation of benzophenone in the presence of methylenenorbornene, methylenenorbornane and norbornene

The experiments described show that triplet benzophenone adds to quadricyclene (**2**) to give 1:1-adducts. It does not, however, add to the doubly homoconjugated diene **1**, despite the fact that only ~54% of quenchings of the ketone triplet by this molecule involve electronic energy transfer.[10] Because of this we have investigated the corresponding reactivity of the singly homoconjugated diene 5-methylenenorbornene (**26**). It was of interest to know (a) whether triplet benzophenone adds to **26** and (b) if so, what, if any, selectivity is shown in terms of the two types of double bond in the molecule. In order to judge the effect of homoconjugation in this system we have also compared the reactivity of **26** with those of 2-methylenenorbornane (**27**) and norbornene (**28**) which serve as models for the double bonds in question in a non-homoconjugated environment.

Nitrogen purged benzene solutions of benzophenone containing an excess of olefin were irradiated until the ketone had been consumed. In each case high chemical yields of 1:1-adducts were produced. These consisted of the oxetanes **29** and **30** from **26**, **31** and **32** from **27** and **33** from **28**. They were isolated by dry column chromatography on alumina in the yields shown in Table 2 (Experiments 9–11). The oxetane pairs **29**/**30** and **31**/**32** could not be separated. Their structures follow from spectral data[g] (Experimental), acid catalysed conversion to **34** and **35** and catalytic hydrogenation of **29**/**30** to **31**/**32** and of **34** to **35**. The reaction of **28** to give **33** has been previously described.[13,14] It is evident from these results that the addition of triplet benzophenone to 5-methylenenorbornene is completely regiospecific although not stereospecific.

Quantum yields and percentage of quenchings leading to adduct

In order to compare relative reactivities with respect to adduct formation we have determined the quantum

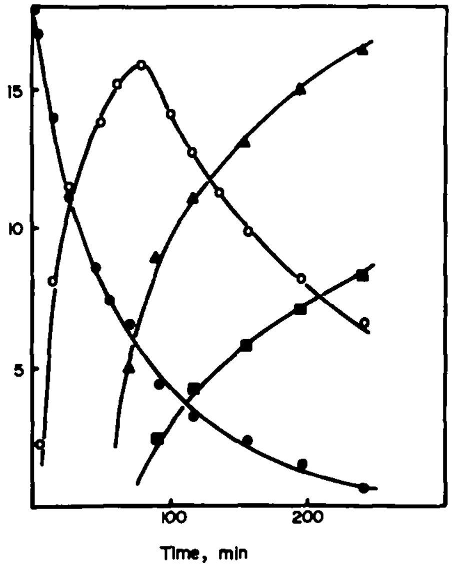


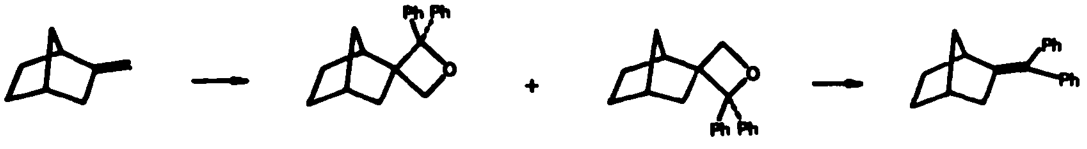
Fig. 3. Irradiation through pyrex of 7-phenacylnorbornadiene (**17**) in C_6D_6. Plots vs time of the NMR integrals (arbitrary units) of the olefinic protons of **17**(●), the cyclopropane protons of **20**(○), the olefinic protons of **21** and **22**(■) and protons of **21** and **22** giving signals between 7.50 and 8.30 τ(▲).

---

[f] Recently Sasaki *et al.*[21] have reported the light-induced addition of 9, 10-phenanthrenequinone and acenaphthenequinone to norbornadiene and quadricyclene. Such quinones are accepted as having lowest n, π^* triplet states.[22] With **2**, adducts of types **5** and **6** were isolated, with **1** only type **5**. No comparison with or reference to our preliminary data[16] was made.

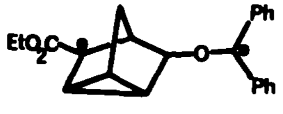
[g] The identification of the major isomers as the *exo* adducts **29** and **31** depends on the shielding effect of the double bond in **29** on the $-CH_2-O$ resonances and a hydrogenation experiment (Experimental section) which shows that the major adducts from **26** and **27** have the same stereochemistry.

26 29 30 34



27 31 32 35

28 33



36

yields ϕ_a shown in Table 4. The rate constants given in Table 1 allow calculation of the maximum possible quantum yield, $\phi_{max} = k_q$ [substrate]/$k_d + k_{eq}$ [ketone] + k_q [substrate]. The experimental quantum yield ϕ_a then gives the percentage of quenchings leading to adduct, $\alpha = \phi_a\ 100/\phi_{max}$ and the effective rate constant for adduct formation, $k_a = k_q\phi_a/\phi_{max}$. These values, which are given in Table 4, serve as a basis for the following discussion.

DISCUSSION AND CONCLUSIONS

(a) *Quadricyclenes*

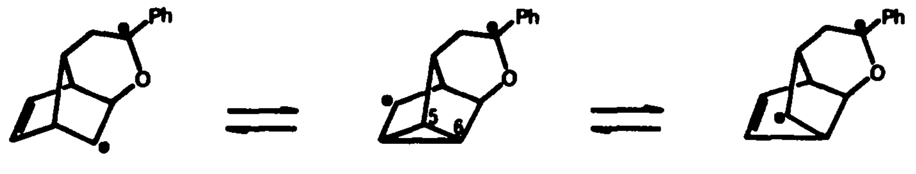
The adducts formed by addition of benzophenone and acetophenone triplets to quadricyclene are clearly the result of *exo* attack. Thus it is not surprising that 7-phenacylquadricyclene (20) for which such attack is mandatory should give corresponding products. We have previously presented evidence[10] which indicates that the quenching of aromatic ketone triplets by quadricyclenes involves charge-transfer induced decay of a triplet exciplex. As shown in Table 4 approximately 1 in 10 of these quenchings leads to 1:1 adducts and therefore a

Table 4. Quantum yield data for adduct formation with triplet benzophenone

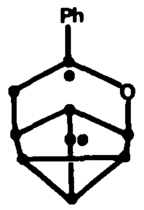
Substrate	ϕ_a [a]	ϕ_{max} [b]	α/%	k_a/l mol^{-1}s^{-1}
quadricyclene (2)	0.09	0.98	9.2	7.6×10^7
2-ethoxycarbonyl quadricyclene (4)	0.08	0.88	9.1	1.1×10^7
5-methylenenorbornene (26)	0.007	0.90	0.78	10.9×10^5
2-methylenenorbornane (27)	0.01	0.80	1.25	7.8×10^5
norbornene (28)	0.004	0.68	0.59	1.9×10^5

[a] 0.05M benzophenone, 0.01M substrate, 313 nm[15].

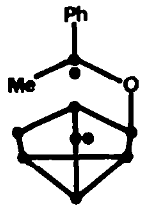
[b] calculated using rate constants in Table 1.



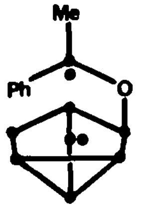
39 38 40



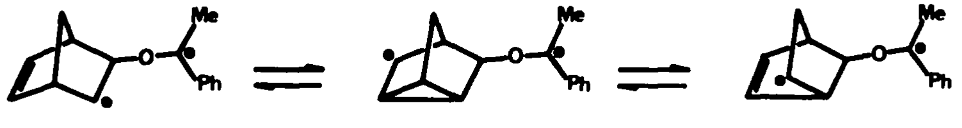
38a



41a



41b



42 41 43

minimum[h] of ~ 10% of quenchings leads to biradical formation. This is an order of magnitude higher than for the olefins 26, 27 and 28 for instance. In addition, it appears that the biradical produced is predominantly that anticipated on stability grounds. This is witnessed by reaction of triplet benzophenone with the ethoxycarbonylquadricyclene (4). Eighty per cent of the isolated products appear to originate from the biradical 36 in which the ester function should stabilise the adjacent radical centre.

A comparison of the intramolecular reaction of 20 with the intermolecular reaction of acetophenone and quadricyclene is of interest, the oxetane:5-ring ether ratios being 2:3 and 3:1 respectively. The initial biradical product of addition of the ketone triplet state of 20 to the quadricyclene nucleus would be 38. Apart from the reflection of CH_2 by O this species is symmetrical (see 38a) and the homoallylic radicals with which it may undergo interconversion (39 and 40) are enantiomeric. Thus, whether or not the oxetane 21 and the 5-ring ether 22 are formed from these latter species or directly from 38 by attack of the benzhydryl like radical on C(5) or C(6) one might anticipate approximately equal amounts of each.

In the case of addition of triplet acetophenone to quadricyclene only one of the epimeric ethers 8a and 8b is formed. The obvious inference is that rotamer 41a of 41 (corresponding to 38a) or the corresponding rotamer of the homoallylic radical 43 forms the sterically most favourable 5-ring ether 8a. Formation of oxetane is sterically less demanding since a mixture of 7a and 7b (3:2 or 2:3) is obtained. Hence the increase in the oxetane to 5-ring ether ratio to 3:1 compared with 2:3 for 20 is understandable.

(b) *Norbornadienes*

It is at first sight surprising that triplet benzophenone does not add to norbornadiene to give adducts since we have previously shown[10] that only 54% of quenching interactions lead to triplet energy transfer. The conclusion has to be that the remaining 46% of quenchings do not lead to *exo* biradical formation. It is possible that for this 46%, decay to ground state reactants involves an endo orientated exciplex in which the ketone triplet is associated with both double bonds (see 44).[i] Such an exciplex could only decay to an *endo* biradical whose formation and/or ring-closure to oxetane would be sterically unfavourable.

(c) *Methylenenorbornene, methylenenorbornane and norbornene*

The k_q values for 2-methylenenorbornane and norbornene in Table 4 suggest that ~ 20% of adducts formed from 5-methylenenorbornene should result from addition to the endocyclic double bond. No such product is formed even though this should be favoured relative to norbornene due to the increased ring strain in 26. The following explanations have been considered.

(a) It is possible that homoconjugative interaction between the double bonds of 26 changes the electron

---

[h] This figure would be greater if fragmentation of biradicals to ground states were significant.

[i] The highest occupied molecular orbital formed by interaction of the π-bonds in this diene is antibonding with respect to that interaction. The interaction depicted in 44 would therefore be symmetry allowed if antarafacial with respect to the singly occupied n(2p) or π* orbitals of the ketone triplet state.

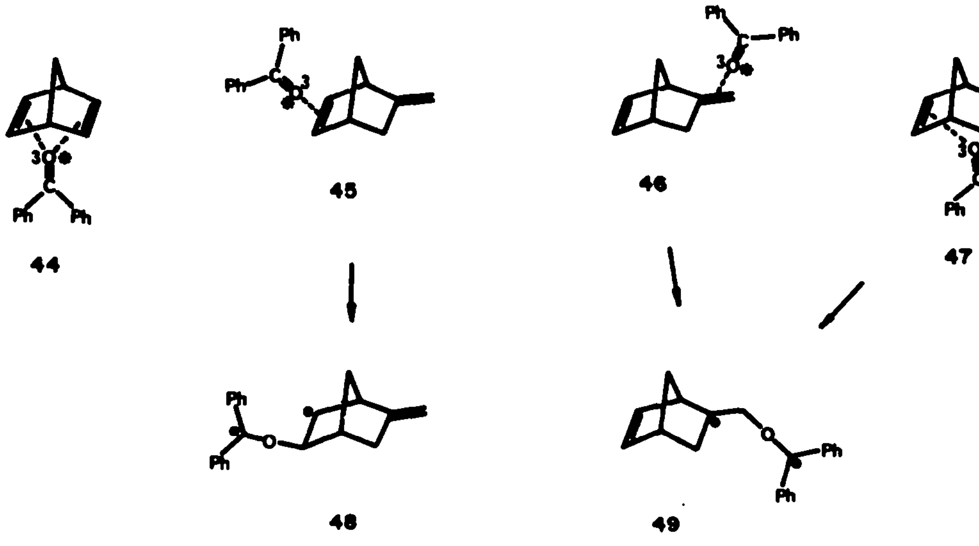


Table 5. Vertical ionisation potentials and ^{13}C chemical shifts

Olefin	IP/± 0.05eV [a]	^{13}C-double bond resonances/ppm.	
		endocyclic	exocyclic
5-methylenenorbornene (26)	8.93, 9.31	134.4, 136.4	103.3, 149.5
2-methylenenorbornane (27)	9.02	-	101.6, 152.4
norbornene (28)	8.95	135.4	-

[a] Reference 23.

availability at the alternative sites of attack. That such interaction occurs is shown by the π-level splitting of 0.31 ± 0.1 eV[23] in **26** compared with **27** and **28** as shown in Table 5. However, the π-ionisation potentials of **27** and **28** are the same within experimental error and they should therefore contribute equally to the highest π-level of **26**; i.e. it is not possible to say that one particular double bond is predominantly associated with the lower ionisation potential. In Table 5 are also shown th ^{13}C chemical shifts of the olefinic carbons of **26**, **27** and **28**. No significant changes are observed for **26** compared with **27** and **28**. The above considerations do not therefore offer a ready explanation of the total regiospecificity of triplet benzophenone addition to **26**.

(b) It is possible that the greater ability of the double bonds in **26** to stabilize a complex by charge-transfer interaction results in an enhanced *selectivity* with respect to subsequent decay processes. Thus, if two distinct *exo* orientated complexes may be formed depending on the double bond involved (**45** and **46**), it is possible that, with respect to the corresponding mono-olefins, production of an intrinsically less stable biradical (e.g. **48**) from the "endocyclic complex" competes less favourably with the alternative modes of decay of that complex than does production of a more stable biradical (**49**) from the "exocyclic complex". The size of the residue $Ph_2\dot{C}$–O– may well cause biradical formation at the exocyclic double bond to be favoured even though more ring strain should be relieved by attack on the endocyclic site.

(c) The most attractive explanation of the regiospecificity under discussion is that, as proposed for norbornadiene, methylenenorbornene (**26**) forms an *endo* orientated complex (**47**) in which both double bonds are associated with the triplet benzophenone.[j] In contrast to **44** this could give a biradical, in which the Ph_2–$\dot{C}$–O– residue does not have the sterically unfavourable endo orientation, i.e. **49**. Closure of the latter, predominantly at the *exo* face, would give the observed products.

Acknowledgement—We thank the Science Research Council for financial support.

EXPERIMENTAL

Benzene (AnalaR grade) was distilled from P_2O_5 after H_2SO_4, water, bicarbonate, water treatment. Benzophenone was recrystallised from EtOH, m.p. 48–49°. Acetophenone was distilled. Norbornadiene and quadricyclene were purified by distillation through a 4 ft steel wool packed column at 19.6 τ, still head temps 52° (norbornadiene) and 68° (quadricyclene). Quadricyclene was prepared by pyrex irraditaion of acetophenone and norbornadiene in ether.[24] 2-Ethoxycarbonylnorbornadiene and 2-ethoxycarbonylquadricyclene were prepared as described.[25] 5-Methylenenorbornene, 2-methylenenorborane and norbornene, the latter as an ether soln (~ 50%), were passed down an alumina column and fractionated from Na. UV spectra were recorded on a Unicam SP800 spectrometer, 95% EtOH as solvent, values in nm (ϵ). IR spectra were recorded on a Perkin-Elmer 257 instrument, values in cm^{-1}. NMR spectra were recorded on a Varian

---

[j] The comments concerning the nature of the interaction in **44** also apply to **47**.

Associates HA 100 (100 MHz) or a Perkin–Elmer R32 (90 MHz) spectrometer, TMS as standard, chemical shifts in ppm. Mass spectra were recorded on an A.E.I. MS12 or MS30 spectrometer at 70 eV unless otherwise stated, values in *m/e*(%), fragment ion peaks ⩾ 25% recorded.

Irradiations leading to product isolation and identification. In the following experiments the reactants in N_2 purged benzene were irradiated through pyrex with a Hanovia 100 W medium pressure mercury arc until the ketone had been consumed (tlc). After solvent removal under reduced pressure products were isolated by dry column chromatography on alumina using benzene as eluent. They are given in order of elution.

(1) Benzophenone (180 mg) and **1**(150 mg) in benzene (70 ml) gave (a) **6**(72 mg, 27%) as a colourless oil which was distilled (0.1 τ, 110°, air bath), ν_{max} (CCl_4) 3090, 3062, 3038, 1080. τ($CDCl_3$) 2.60 – 3.00 (10 H; m), 3.94 (1 H; q; 7 and 2 Hz), 4.37 (1 H; o; 7, 3, and 1 Hz), 5.80 (1 H; t; ~ 1 Hz), 7.08 (1 H; broad s), 7.17 (1 H; d; 6 Hz), 7.38 (1 H; broad s), 8.29 (1 H; q; 12 and 5 Hz), 9.16 (1 H; q; 12 and 6 Hz). *m/e* 274 (M^+, 42), 256 (37), 205 (25), 204 (35), 178 (28), 167 (98), 165 (100), 152 (40), 115 (35), 105 (27), 91 (50), 81 (27), 77 (58). (b) the oxetane **5** (162 mg, 60%), as a white crystalline solid, m.p. 142–144° (MeOH), λ_{max} 255 (575). ν_{max} (CCl_4) 3050, 3010, 960. τ($CDCl_3$) 2.50–3.00 (10 H; m), 3.91 (1 H; q; 4 and 2 Hz), 4.20 (1 H; q; 4 and 2 Hz), 5.50 (1 H; d; 5 Hz), 7.02 (2 H; broad s), 7.26 (1 H; d; 5 Hz), 8.22 (1 H; d; 8 Hz), 8.83 (1 H; d; 8 Hz). *m/e* 274 (M^+, 44), 256 (29), 209 (70), 208 (48), 207 (91), 204 (37), 192 (25), 183 (30), 178 (50), 167 (86), 165 (91), 152 (40), 115 (38), 105 (68), 102 (28), 92 (84), 91 (100), 77 (82), 66 (47). (Found: C, 87.3; H, 6.6. Calc. for $C_{20}H_{18}O$: C, 87.5; H, 6.8%).

(2) Benzophenone (180 mg) and **2**(150 mg) in benzene (70 ml) gave **6**(26%) and **5**(55%).

(3) Acetophenone (95 mg) and **1**(217 mg) in benzene (60 ml) gave (a) an unidentified minor adduct (8 mg, 5%) as an oil, ν_{max}(CCl_4) 3050, 1125, 1000. *m/e* 212 (M^+, 3), 168 (30), 167 (36), 58 (45), 43 (100). (b) the ether **8a** (28 mg, 17%) as an oil, λ_{max} 252 (575). ν_{max} (CCl_4) 3080, 1050. τ($CDCl_3$) 2.70 – 2.90 (5 H; m), 3.88 (1 H; q; 6 and 3 Hz), 4.23 (1 H; 0; 6.3 and 1 Hz), 5.84 (1 H; t; ~ 1 Hz), 6.55 (1 H broad s), 7.49 (1 H;broad m), 7.76 (1 H; q; 6 and 2 Hz), 8.54 (3 H; s), 8.60 (1 H; q; 12 and 5 Hz), 9.34 (1 H; q; 12 and 6 Hz). *m/e* 212 (M^+, 13), 167 (90), 129 (25), 105 (60), 91 (35), 77 (25), 58 (48), 43 (100). (c) a mixture of the oxetanes **7a** and **7b**, 3:2 or 2:3 (104 mg, 62%) as an oil, λ_{max} 250 (437). ν_{max} (CCl_4) 3060, 960. τ($CDCl_3$) 2.50–2.90 (5 H; m), 3.88 (1 H; m), 4.18 (1 H; m), 5.47 (~ 0.6 H; d; 6 Hz), 5.61 (~ 0.4 H; d; 6 Hz), 6.98 (1 H; broad s), 7.32 (~ 0.6 H; broad s), 7.47 (~ 0.4 H; broad s), 7.53 (~ 0.6 H; d; 6 Hz), 7.73 (~ 0.4 H; d; 6 Hz), 8.32 (1.8 H; s),[k] 8.52 (1.2 H, s),[k] 8.90 (1 H; d; 10 Hz). *m/e* 212 (M^+, 26), 183 (26), 147 (35), 145 (29), 141 (26), 129 (30), 115 (26), 105 (60), 91 (75), 43 (100).

(4) Acetophenone (95 mg) and **2**(230 mg) in benzene (60 ml) gave the above minor product (4%), **8a**(21%) and a mixture of **7a** and **7b** (57%).

(5) Benzophenone (17 mg) and **3**(30 mg) in benzene (70 ml) gave the adducts described under experiment (6), tlc identification only.

(6) Benzophenone (17 mg) and **4**(30 mg) in benzene (70 ml) gave (a) **9**(12 mg, 35%), m.p. 138–139° (60/80 petrol), λ_{max} 223 (7000). ν_{max}(CCl_4) 3050, 1715, 965. τ($CDCl_3$) 2.40–2.90 (10 H; m), 3.00 (1 H; d; 3 Hz), 5.30 (1 H; d; 5 Hz), 5.89 (2 H; q; 8 Hz), 6.56 (1 H; s), 6.82 (1 H; broad s), 7.12 (1 H; d; 5 Hz), 8.08 (1 H; d; 10 Hz), ~ 8.66 (1 H; d; 10 Hz), 8.76 (3 H; t; 8 Hz). *m/e* 346 (M^+, 20), 209 (45), 208 (85), 207 (100), 178 (25), 165 (40), 164 (40), 135 (25), 119 (25), 105 (40), 91 (60), 77 (35). (b) a mixture of **10** and **11** (~ 1:1) as a colourless oil (~ 6 mg), τ($CDCl_3$) 2.40–2.90 (10 H; m), 3.00 (~ 0.5 H; d; 3 Hz), 3.32 (~ 0.5 H; d; 3 Hz), 5.34 (~ 0.5 H; d; 5 Hz), 5.66 (~ 0.5 H; t; 1 Hz), 5.75–6.02 (2 H; two overlapping q's; 8 Hz), 6.56 (1 H; broad s), 6.81 (~ 0.5 H; broad s), 6.96 (~ 0.5 H; d; 6 Hz), 7.08 (~ 0.5 H; d; 5 Hz), 7.17 (~ 0.5 H; m), 8.04–8.30 (1 H; m), 8.60–8.88 (3 H; two overlapping t's; 8 Hz), ~ 9.10 (~ 0.5 H; m). *m/e* 346 (M^+, 27), 208 (30), 207 (100), 183 (45), 167 (58), 165 (43), 105 (65), 91 (52), 77 (43).

(7) Acetophenone (22 mg) and **1**(33 mg) in benzene (60 ml) gave a mixture of adducts only two of which could be isolated in homogenous form, (a) τ($CDCl_3$) 2.50–2.90 (5 H; m), 3.02 (1 H; d; 3 Hz), 5.35 (1 H; d; 5 Hz), 5.84 (2 H; q; 8 Hz), 6.22 (1 H; broad s), 7.14 (1 H; broad s), 7.45 (1 H; d; 5 Hz), 8.16 (1 H; d; 8 Hz), 8.31 (3 H; s), 8.44 (1 H; d; 8 Hz), 8.72 (3 H; t; 8 Hz). *m/e* 284 (M^+, 10), 164 (75), 147 (75), 146 (75), 145 (100), 138 (60), 110 (60), 91 (54), 79 (25). (b) τ($CDCl_3$) 2.50–2.90 (5 H; m), 3.00 (1 H; d; 3 Hz), 5.48 (1 H d; 5 Hz), 5.90 (2 H; q; 8 Hz), 6.56 (1 H; broad s), 6.79 (1 H; broad s), 7.42 (1 H; d; 8 Hz), 7.65 (1 H; d; 5 Hz), 8.28 (1 H; d; 8 Hz), 8.48 (3 H; s), 8.74 (3 H; t; 8 Hz). *m/e* 284 (M^+, 5), 183 (35), 164 (75), 147 (100), 146 (25), 145 (85), 138 (25), 121 (25), 105 (30), 91 (60), 79 (25).

(8) Acetophenone (22 mg) and **4**(33 mg) in benzene (60 ml) gave the adducts described under experiment (7), tlc identification only.

(9) Benzophenone (142 mg) and **26**(156 mg) in benzene (70 ml) gave (a) an oil which was distilled (0.6 τ, 125–130°, air bath) to give a mixture (155 mg) of **29** and **30** (~ 4:1), λ_{max} 255 (1259). ν_{max} (CCl_4) 3060, 3010, 990. τ($CDCl_3$) 2.50–2.90 (10 H; m), 3.88 (1 H; dd; 4 and 3 Hz), 4.14 (1 H; dd; 4 and 3 Hz), 5.38 (0.2 H; d; 6 Hz), 5.60 (0.2 H; d; 6 Hz), 5.68 (0.8 H; d; 6 Hz), 5.98 (0.8 H; d; 6 Hz), 7.22 (2 H; broad s), 7.88–9.00 (4 H). *m/e* 288 (M^+, 2), 106 (60), 105 (57), 91 (100), 78 (60), 77 (52), 66 (53), 58 (30), 43 (97). (Found: C, 87.5; H, 6.8. Calc. for $C_{21}H_{20}O$: C, 87.5; H, 7.0%). (b) an oil (14 mg) with spectral properties indicating 2:1 adducts of benzophenone and methylenenorbornene, λ_{max} 256 (1995). ν_{max} (CCl_4) 3060, 3012, 975. NMR complex. *m/e* 470 (M^+, 1), 106 (26), 105 (100), 91 (34), 77 (36). *m/e* (14 eV) 470 (M^+, 7), 288 (100), 258 (50), 105 (61).

(10) Benzophenone (150 mg) and **27**(112 mg) in benzene (75 ml) gave a mixture (161 mg) of **31** and **32** (~ 6:1), ν_{max}(CCl_4) 3080, 3055, 3020, 980. τ($CDCl_3$) 2.30–2.90 (10 H), 5.25 (~ 0.15 H; d; 5 Hz), 5.30 (~ 0.85 H; d; 5 Hz), 5.74 (~ 0.85 H; d; 5 Hz), 5.83 (~ 0.15 H; d; 5 Hz), 7.50–9.20 complex. *m/e* 290 (M^+, 2), 260 (60), 231 (34), 183 (100), 105 (52), 79 (32), 77 (40), 66 (30).

(11) Benzophenone (790 mg) **28**(630 mg) in benzene (70 ml) gave a product which was distilled (0.05 τ, 130–135°, air bath) to give the known **33** (965 mg), m.p. 120–123° (EtOH), Lit. 121°[13] and 128–129°.[14] ν_{max}(CCl_4) 3078, 3055, 3010, 978. τ($CDCl_3$) 2.40–2.75 (10 H), 5.25 (1 H; d; 5 Hz), 7.10 (1 H; d; 5 Hz), 7.62 (2 H; broad s), 7.90–9.10 (6 H). *m/e* 276 (M^+, 53), 248 (52), 206 (32), 205 (84), 204 (36), 203 (28), 191 (40), 183 (60), 180 (96), 168 (92), 167 (75), 165 (69), 115 (46), 105 (44), 91 (100), 77 (36), 66 (52).

(12) 7-Phenacylnorbornadiene (**17**, 21 mg) in benzene (100 ml) led to complete loss of starting material within 2 hr. After solvent removal under vacuum preparative tlc on silica gel with benzene as eluent (4 runs) gave the cyclobutane derivative **22** as an oil (10 mg), ν_{max} 3060, 1320, 1065. τ($CDCl_3$) 2.70 (m, 5 H), 3.97 (1 H; dd; 7 and 3 Hz), 4.18 (1 H; dd; 7 and 3 Hz), 5.53 (1 H; broad s), 7.00–7.25 (m, 3 H), 7.49 (1 H; dd; 11 and 8 Hz), 8.00 (m, 1 H), 8.16 (1 H; d; 11 Hz). *m/e* 210 (M^+, 3), 105 (70), 91 (27), 77 (40), 58 (100), 43 (100).

(13) *syn*-7-Phenacylnorbornene (**18**, 42 mg) in benzene (100 ml) led to complete loss of starting material within 2 hr with concomitant formation of a single product (tlc). Removal of solvent gave an oil identified as essentially pure **23**, ν_{max} (CCl_4) 3055, 3022, 985. τ(CCl_4) 2.60–3.00 (5 H), 5.88 (1 H; q; 6 and 1 Hz), 6.75 (1 H; m), 7.40–8.90 (9 H).

(14) *anti*-7-Phenacylnorbornene (**19**, 24 mg) in benzene (50 ml) gave no reaction after 4 hr.

Kinetic irradiations. In the following experiments irradiations were performed with a Hanovia 100 W medium pressure mercury arc. Unless otherwise stated benzene solutions of reactants were N_2 purged and irradiated through pyrex.

(15) *Benzophenone and norbornadiene* (**1**). Pyrex tubes each containing solns (9 ml) of benzophenone (18 mg) and *n*–nonane (8 mg) in purified **1** were freeze-thaw degassed (10 cycles), sealed and irradiated on a merry-go-round apparatus. Solns were removed at 20 min intervals and analysed by glc. Quadricyclene was monitored against internal *n*-nonane (3 ft, 14% Apiezon L on Chromosorb A, 85°, 10 psi), benzophenone against added 2-

---

[k] These signals overlap with the signals due to the C(7)-hydrogens which are *anti* with respect to the double bond (total 1 H).

naphthaldehyde (3 ft, 4% polyethylene glycol adipate on Chromosorb G, 170°, 10 psi) (see Fig. 2).

(16) *Benzophenone and quadricyclene* (2). A soln of benzophenone (3.66 g), 2(497) mg) and n-nonane (1.28 g) in benzene (80 ml) was irradiated. The decay of 2, monitored against n-nonane by glc (6 ft, 14% Apiezon L on Chromosorb A, 70°, 10 psi), was linear up to >50% conversion.

(17) *Acetophenone and norbornadiene* (1). An experiment essentially identical to (15) was carried out apart from the use of tetradecane as internal standard for acetophenone (3 ft, 20% diethyleneglycol succinate on Chromosorb W, 120°, 10 psi).

(18) *Acetophenone and quadricyclene* (2). A soln of acetophenone (2.4 g), 2(470 mg) and n-nonane (1.28 g) in benzene (80 ml) was irradiated and analysed as for experiment (16) with the same result.

(19) *Benzophenone and 2-ethoxycarbonylnorbornadiene* (3). A soln of benzophenone (29 mg), 3(29 mg) and n-propyl laurate (25 mg) was irradiated at 313 nm.[15] The decay of 3 and the formation of 4, monitored against n-propyl laurate by glc (3 ft, 20% diethyleneglycol succinate on Chromosorb W, 120°, 10 psi), proceeded with identical zero-order rates up to 70% conversion.

(20) *Benzophenone and 2-ethoxycarbonylquadricyclene* (4). A soln of benzophenone (2.06 g), 4(1.3 g) and n-propyl laurate (0.68 g) in benzene (80 ml) was irradiated. The decay of 4, monitored by glc (3 ft, 4% polyethyleneglycol adipate on Chromosorb G, 100°, 10 psi), was linear up to 50% conversion.

(21) *Acetophenone and 2-ethoxycarbonylnorbornadiene* (3). A soln of acetophenone (1.44 g), 3(0.33 g) and n-propyl laurate (0.48 g) in benzene (200 ml) was irradiated at 313 nm.[15] Decay of 3 and formation of 4, analysed as for experiment (19), proceeded at identical rates up to 60% conversion (Fig. 1).

(22) *Acetophenone and 2-ethoxycarbonylquadricyclene* (4). A soln of acetophenone (1.17 g), 4(105 mg) and n-propyl laurate (0.99 g) in benzene (60 ml) was irradiated. Decay of 4, analysed as for experiment (20), was linear up to 50% conversion.

(23) 7-*Phenacylnorbornadiene* (17). A freeze-thaw (8 cycles) degassed soln of 17(5.0 mg) in hexadeuteriobenzene in a sealed pyrex NMR tube was irradiated and the reaction monitored (see Fig. 3).

Quantum yields. Reaction and actinometer (benzophenone/benzhydrol in benzene) solutions were irradiated on a merry-go-round in sealed pyrex tubes which had been freeze-thaw degassed (10 cycles). The incident light consisted of an envelope centred at 313 nm obtained by filtering the light of a Hanovia 550 W medium pressure mercury arc with a soln of potassium chromate (0.002 mol l^{-1}) in 1% K_2CO_3aq.[15] All the incident light was absorbed by the benzophenone and conversions were less than 10%. Solns were analysed by glc using as standards either 2-naphthaldehyde on 3 ft, 4% polyethylene glycol adipate on Chromosorb G, 170°, 10 psi or n-nonane on 3 ft, 14% Apiezon L on Chromosorb A, 85°, 10 psi.

Ring opening of oxetanes

(24) *Oxetanes 29/30 to 5-diphenylmethylenenorbornene* (34). A soln of 29/30 (55 mg) in benzene (10 ml) was stirred at room temp. with silica gel (15 mg) for 5 hr. Normal work up gave 34(46 mg), m.p. 73–75° (EtOH), λ_{max} 252 (13180). ν_{max} (CCl_4) 3059, 3010, 1595. τ($CDCl_3$) 2.80–3.00 (10 H), 3.95 (2 H; m), 6.68 (1 H; broad s), 7.12 (1 H; broad s), 7.55 1 H; dd; 15 and 4 Hz), 8.15–8.70 (3 H). *m/e* 258 (M^+, 86), 204 (31), 182 (100), 181 (98), 165 (89), 115 (38), (Found: C, 92.7; H, 7.1. Calc. for $C_{20}H_{18}$: C, 93.0; H, 7.0%).

(25) *Oxetanes* 31/32 *to 2-diphenylmethylenenorbornane* (35). Treatment of 31/32 (45 mg) as for experiment (24) gave 35 (39 mg) as an oil, λ_{max} 252 (12590). ν_{max} (CCl_4) 3070, 3050, 3010, 1600. τ($CDCl_3$) 2.65–2.75 (10 H), 7.10 (1 H; broad s), 7.40–9.00 (9 H). *m/e* 260 (M^+, 100), 231 (56), 193 (28), 180 (45), 165 (41), 105 (28), 91 (26), 77 (28), 58 (82).

(26) *Oxetane 23 to aldehydes 24 and 25.* Distillation of 23 (40 mg; 0.1 τ, 80°, air bath) gave a virtually quantitative yield of 24 as an oil (38 mg), ν_{max} (film) 3020, 3010, 2700, 1720. τ(CCl_4) 0.22 (1 H; d; 1 Hz), 2.50–2.90 (5 H; m), 4.02 (1 H; q; 1.5 Hz), 6.30–7.65 (5 H), 8.05—8.20 (4 H). *m/e* 212 (M^+, 14), 183 (56), 155 (81), 142 (44), 105 (43), 77 (27), 69 (35). Attempted separation from traces of 18 on a silica gel plate gave the epimeric aldehyde 25, τ($CDCl_3$) 0.28 (1 H; d; 1 Hz), 2.40–2.90 (5 H; m), 3.98 (1 H; m), 6.30–7.60 (5 H), 7.80–8.40 (4 H).

Hydrogenations. In the following experiments the reactant in EtOH was shaken under H_2 with PtO_2 until 1 mole of H_2 had been absorbed. The mixture was filtered through Celite 545, the EtOH concentrated and the whole subjected to ether/water work up. The organic product was subjected to dry column chromatography on alumina with benzene as eluent.

(27) *Oxetanes 29/30 to* 31/32. A ~4:1 mixture of 29 and 30 (150 mg) from experiment (9) with PtO_2 (56 mg) in EtOH (45 ml) gave after 30 min hydrogenation a ~4:1 mixture of 31 and 32 (143 mg). Spectral data were essentially identical to those of the 31/32 mixture from experiment (10) apart from the product ratio.

(28) *5-Diphenymethylenenorbornene* (34) *to 2-diphenylmethylenenorbornane* (35). The olefin 35 (42 mg) and PtO_2 (12 mg) in EtOH (20 ml) gave after 40 min hydrogenation an oil (33 mg) identical in all respects to 35 obtained in experiment (25).

(29) *Oxetane 5 to oxetane* 33. Oxetane 5 (40 mg) and PtO_2 (15 mg) in EtOH (25 ml) gave after 30 min hydrogenation a crystalline solid (38 mg). It's m.p. after recrystallisation from EtOH, 120–122°, was undepressed by admixture with a sample from experiment (11).

Synthesis of 7-phenacylnorbornadiene

(30) 7-*Norbornadienylacetic acid.* Crude[j] ethyl-7-norbornadienylacetate (103 mg) and NaOH (0.5 g) in water (5 ml) were refluxed for 30 min. Work up for acidic material using ether/HCl/$CHCl_3$ gave after distillation a product (52 mg) consisting mainly of 7-norbornadienylacetic acid, ν_{max} (film) 3680–2300 (broad), 1715. τ(CCl_4)–1.15 (1 H; s), 3.27 (2 H; t; 2 Hz), 3.48 (2 H; t; 1 Hz), 6.60 (2 H; m), 7.20 (1 H; t; 8 Hz), 7.65 (2 H; d; 8 Hz). *m/e* 150 (M^+, 16), 105 (37), 91 (100), 80 (29), 79 (27). The only observable impurity in this material was ~20% 7-cycloheptatrienylacetic acid (NMR).

(31) 7-*Phenacylnorbornadiene* (17). To crude 7-norbornadienylacetic acid (74 mg, 0.5 mmoles) from experiment (30) in ether (10 ml) at −55° was added PhLi in benzene/ether (1 ml, 2.1 mmoles). Addition of water after 1 hr and ether extraction gave a product which was subjected to chromatography on silica gel using hexane, acetone, triethylamine (90:8.8:1.2) as eluent. This gave (a) 7-phenacylnorbornadiene (15 mg), m.p. 32–36° (not recrystallised), λ_{max} 243 (16,000), 277 (830), 315 (70). ν_{max} (CCl_4) 3060, 3010, 1690, 1600. τ(C_6D_6) 2.10–2.40 (2 H; m), 2.70–3.10 (3 H; m), 3.29 (2 H; t; ~1.5 Hz), 3.56 (2 H t; ~1.5 Hz), 6.70 (2 H; m), 6.90 (1 H; broad t; 7 Hz), 7.24 (2 H; d; 7 Hz). τ(CCl_4) 2.00–2.30 (2 H; m), 2.40–2.90 (3 H; m), 3.19 (2 H; t; ~1.5 Hz), 3.40 (2 H; t; ~1.5 Hz), 6.54 (2 H; m), 7.02 (3 H; m). *m/e* 210 (M^+, 7), 105 (100), 91 (32), 77 (81). (Found: C, 85.4; H, 6.9. Calc. for $C_{15}H_{14}O$: C, 85.7; H, 6.7%). (b) 7-phenacylcycloheptatriene (7 mg) as an oil, ν_{max} (CCl_4) 3021, 3000, 1680, 1600. τ(C_6D_6) 2.10–2.40 (2 H;m), 2.70–3.10 (3 H; m), 3.53 (2 H; t; 3 Hz), 3.80–4.10 (2 H; m), 4.85 (2 H; dd; 10 and 5 Hz), 7.05 (2 H; d; 8 Hz), 7.20–7.60 (1 H; m). *m/e* 210 (M^+, 7), 105 (62), 91 (100), 77 (74), 51 (36). (c) a mixture of 2-7′-norbornadienyl-and 2–7′-cycloheptatrienyl-1, 1-diphenylethanol (~1:1) as an oil (30 mg), ν_{max} 3450 (broad), 3045, 3005. τ ($CDCl_3$) 2.60–3.00 (m; 10 H), 3.40 ($\sim 0.5 \times 2$ H; t; 3 Hz), 3.52 ($\sim 0.5 \times 2$ H + 0.5×2 H; m), 3.98 ($\sim 0.5 \times 2$ H; m), 4.90 ($\sim 0.5 \times 2$ H; dd; 10 and 6 Hz), 6.98 ($\sim 0.5 \times 2$ H; broad s), 7.31 ($\sim 0.5 \times 2$ H; d; 7 Hz), 7.35–8.40 (3 H). *m/e* 270 (M^+, 33), 183 (65), 180 (54), 105 (100), 91 (66), 77 (60).

Synthesis of syn and anti-7-phenacylnorbornene

(32) 7-*Phenacylidenenorbornene.* The Wittig reagent prepared from phenacyl bromide and triphenylphosphine[27] (14 g) and norbornen-7-one[28] (3.5 g) were refluxed in toluene (200 ml) for 3 days. The toluene was removed under vacuum and the residue extracted with pentane which, after passage down a short silica gel column and evaporation, yielded an oil which was distilled (0.2 τ, 115–120°, air bath) to give 7-phenacylidenenorbornene (1.02 g),

---

[j] In our hands the literature procedure[26] gave a product containing ~20% of the corresponding 7-substituted cycloheptatriene (NMR).

λ_{max} 266 (21,000), λ_{inf} 330 (236). ν_{max} (film) 3061, 1686, 1640. $\tau(CDCl_3)$ 1.91–2.29 (2 H; m), 2.36–2.71 (3 H; m), 3.73 (3 H; m), 5.86 (1 H; broad s), 6.87 (1 H; broad s), 8.00–9.00 (4 H). *m/e* 210 (M^+, 33), 182 (100), 154 (29), 105 (89), 77 (68).

(33) *syn-and anti-2-7'-Norbornenyl*-1-*phenylethanol*. $NaBH_4$ (2.4 g) was added to a soln of 7-phenacylidenenorbornene (3.0 g) in pyridine (30 ml) and the mixture refluxed for 30 min. Addition of a soln of potassium iodate (1.0 g) in water (150 ml) and stirring for 15 min followed by ether extraction, acid-water washing, etc. gave an oil (2.8 g) apparently homogenous by tlc. Purification of a sample on a silica gel plate using toluene as eluent followed by distillation (0.1 τ, 90°, air bath) gave a ~ 1:1 mixture of the *syn*-and *anti*-2-7'-norbornenyl-1-phenylethanols which slowly crystallised, m.p. 35–43°, ν_{max} (nujol) 3245 (broad), 3065. $\tau(CDCl_3)$ 2.70 (5 H; m), 3.96 (~ 0.5 × 2 H; t; 2 Hz), 4.13 (~ 0.5 × 2 H; t; 1.5 Hz), 5.30–5.60 (1 H; m), 7.25–7.62 (2 H), 8.10–8.60 (5 H), 8.90–9.15 (2 H; m). *m/e* 214 (M^+, 12), 196 (44), 168 (30), 155 (100), 120 (31), 107 (90), 105 (60), 104 (28), 92 (33), 91 (34), 80 (59), 79 (59), 77 (37).

(34) *syn-and anti-7-Phenacylnorbornene* (**18** and **19**). The crude product from experiment (33) was oxidised with Jones reagent to give a product (1.97 g). Dry column chromatography of this product (1.3 g) on a silver nitrate-silica gel column using toluene as eluent gave **18** as an oil (495 mg) which was distilled (0.1 τ, 60°, air bath), λ_{max} 243 (10800), 277 (957), 315 (72). ν_{max} (film) 3050, 1670, 1600. $\tau(CDCl_3)$ 2.00–2.20 (2 H; m), 2.40–2.60 (3 H; m), 4.10(2 H; t; 1 Hz), 7.05 (2 H; d; 8 Hz), 7.25 (2 H; m), 7.84 (1 H; t; 8 Hz), 8.10–8.40 (2 H; m), 8.90–9.10 (2 H; m). *m/e* 212 (M^+, 17), 105 (100), 77 (53). Further elution with $EtOAc_2$ gave an oil (630 mg) which was distilled (0.1 τ, 60°, air bath) to give **19** which crystallised, m.p. 45–46.5°, λ_{max} 243 (14230), 282 (1173), 314 (92). ν_{max} (film) 3050, 1670, 1600. $\tau(CDCl_3)$ 2.00–2.16 (2 H; m), 2.40–2.60 (3 H; m), 3.94 (2 H; t; 1.5 Hz), 7.28 (2 H; d; 8 Hz), 7.36 (2 H; m), 7.90 (1 H; t; 8 Hz), 8.15–8.45 (2 H; m), 8.85–9.10 (2 H; m). *m/e* 212 (M^+, 2), 196 (27), 105 (100), 77 (26). Dinitrophenylhydrazone m.p. 198–200° (EtOH).

REFERENCES

[1] E. Paterno and G. Chieffi, *Gazz. Chim. Ital.* **39**, 341 (1909).

[2] G. Büchi, C. G. Inman and E. S. Lipinsky, *J. Am. Chem. Soc.* **76**, 4327 (1954).

[3] D. R. Arnold, *Advances in Photochem.* **6**, 330 (1968).

[4] R. A. Caldwell and S. P. James, *J. Am. Chem. Soc.* **91**, 5184 (1969).

[5] R. A. Caldwell, *Ibid.* **92**, 1439 (1970).

[6] R. A. Calwell, G. W. Sovocool and R. P. Gajewski, *Ibid.* **95**, 2549 (1973).

[7] I. E. Kochevar and P. J. Wagner, *Ibid.* **94**, 3859 (1972).

[8] A. Gupta and G. S. Hammond, *Ibid.* **98**, 1218 (1976).

[9] G. S. Hammond, P. Wyatt, C. D. de Boer and N. J. Turro, *Ibid.* **86**, 2532 (1964).

[10] A. J. G. Barwise, A. A. Gorman, R. L. Leyland, M. A. J. Rodgers and P. G. Smith, *Ibid.* **100**, 1814 (1978).

[11] A. J. G. Barwise, A. A. Gorman and M. A. J. Rodgers, *J. Photochem.* **6**, 11 (1978).

[12] G. M. Barrow and S. Searles, *J. Am. Chem. Soc.* **75**, 1175 (1953).

[13] D. Scharf and F. Korte, *Tetrahedron Letters* 821 (1973).

[14] D. R. Arnold, R. L. Hinman and A. H. Glick, *Ibid.* 1425 (1964).

[15] N. J. Turro and P. Wriede, *J. Am. Chem. Soc.* **92**, 320 (1970).

[16] A. A. Gorman and R. L. Leyland, *Tetrahedron Letters* 5345 (1972).

[17] T. Kubota, K. Shima and H. Sakurai, *Chemistry Letters* 343 (1972).

[18] A. J. G. Barwise, A. A. Gorman and C. T. Parekh, to be published.

[19] R. R. Sauers, W. Schinski and M. M. Mason, *Tetrahedron Letters* 79 (1969).

[20] W. G. Dauben and R. L. Cargill, *Tetrahedron* **15**, 197 (1961).

[21] T. Sasaki, K. Kanematsu, I. Ando and O. Yamashita, *J. Am. Chem. Soc.* **99**, 871 (1977).

[22] J. M. Bruce, *Quart. Rev. Chem. Soc.* **21**, 405 (1967).

[23] S. A. Cowling, R. A. W. Johnstone, A. A. Gorman and P. G. Smith, *J. Chem. Soc. Chem. Comm.* 627 (1973).

[24] C. D. Smith, *Org. Synth.* **51**, 133 (1971).

[25] J. B. Sheridan, Ph. D. Thesis, Manchester, (1971).

[26] R. S. Bly, R. K. Bly, G. B. Konizer and S. P. Jindal, *J. Am. Chem. Soc.* **98**, 2953 (1976).

[27] A. J. Speziale and K. W. Ratts, *Ibid.* **85**, 2790 (1963).

[28] P. G. Gassman and J. C. Marshall, *Org. Synth.* **48**, 25, 68 (1968).