way, benzhydryl methyl ether possesses singlet peaks at δ 3.29 (3 H) and 5.11 (1 H).

Photooxidation of 9-Diazofluorene (6) in the Presence of MeOH. A similar procedure showed the formation of a 34% yield of 9-hydroperoxy-9-methoxyfluorene (4, R_2 = 9-fluorenyl) in addition to 9-methoxyfluorene (3%) and fluorenone (63%).

The purification by the extraction with 0.1% NaOH, neutralization with AcOH, and extraction with CH_2Cl_2 gave pure (by NMR) 9-hydroperoxy-9-methoxyfluorene; we could not crystallize it. Its NMR spectra (CCl_4) δ 3.35 (singlet, 3 H) 7.3–7.8 (multiplet, 8 H), and 8.7

(broad s, 1 H) are different from those of 9-methoxyfluorene with δ 3.05 (s, 3 H) and 5.59 (s, 1 H),[42] supporting the α-methoxy hydroperoxide structure. The hydroperoxide is reduced by KI to fluorenone at 50 °C in $AcOH-MeOH-H_2O$ (1:1:2).

Acknowledgment. We are grateful to Dr. Kimihiko Hirao for his aid in the calculation of MINDO/3 and to Dr. Kohtaro Tomizawa for his aid in the measurement of GC–MS spectra. The MO calculations were carried out on a FACOM-M200 of the Nagoya University Computational Center.

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Monoradical Rearrangements of the 1,4-Biradicals Involved in Norrish Type II Photoreactions

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Abstract: The photochemistry of α-allylbutyrophenone (α-AB) and that of γ-cyclopropylbutyrophenone (γ-CB) both reveal that the 1,4-biradicals generated by triplet-state γ-hydrogen abstraction undergo typical radical rearrangements in competition with their more normal type II reactions. From α-AB, 2-phenyl-2-norbornanol is formed in $^1/_{24}$th the combined yield of 1-phenyl-4-penten-1-one and 1-phenyl-2-allylcyclobutanol. Its formation is explained by a 5-hexenyl-to-cyclopentylmethyl rearrangement of the 1,4-biradical, with a rate constant of 5×10^5 s⁻¹. From γ-CB, 1-phenyl-4-hepten-1-one and 1-phenyl-4-cycloheptenol together are formed in double the yield of acetophenone. Their formation is explained by a cyclopropylcarbinyl-to-allylcarbinyl rearrangement of the 1,4-biradical, with a rate constant of 2×10^7 s⁻¹. In both cases, the rearrangement percentages are what would be predicted if the biradicals have the same 35–50-ns lifetime measured for other ketones and if they rearrange with the same rate constants characteristic of monoradicals. Triplet γ-CB decays only 1.5 times faster than triplet γ-isopropylbutyrophenone, indicating that there is at most a small enhancement of the γ-hydrogen abstraction rate by cyclopropyl conjugation. Triplet α-AB decays 100 times faster than triplet butyrophenone, 99% representing internal quenching by the β-vinyl group ($k = 8 \times 10^8$ s⁻¹). Bicyclic oxetanes are formed in quantum yields of only 0.01. No oxetanes were isolated, only rearranged unsaturated alcohols and aldehydes.

Introduction

Since we first successfully trapped the 1,4-biradicals known to be involved in Norrish type II photoelimination and cyclization,[2] there has been considerable interest in the factors which influence the behavior of such intermediates.[3] The fact that the first trapping reaction involved hydrogen atom abstraction from a thiol prompted two related questions: (1) Do monoradical reactions of biradicals occur with the same rate constants as those of simple radicals? (2) If so, can competitive monoradical reactions be used to determine biradical lifetimes?

In the expectation that the answer to the first question is "yes", we prepared two ketones which, upon triplet state γ-hydrogen abstraction, would form biradicals which could undergo characteristic free-radical rearrangements. We have already communicated a positive result for α-allylbutyrophenone (α-AB).[4] This paper reports our complete results for both ketones.

About the time we finished these experiments, Scaiano reported the first direct flash spectroscopic determination of type II biradical lifetimes.[5] This independent experimental capability minimizes
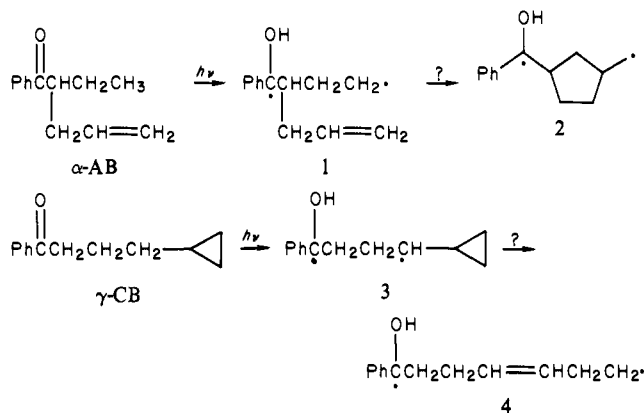
the importance of the second question presented above but allowed us to focus on the more fundamental first question. Coupled with Beckwith's recent extensive study of structural effects on free-radical rearrangement rates,[6] our results allow the conclusion that

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Scheme I

5 (0.0014)

6 (0.0010)

7 (0.0001)   0.0019   0.0042

0.0026
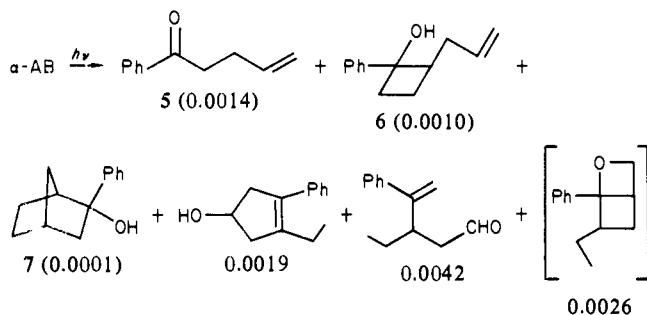
radical rearrangements of biradicals do indeed occur with the same rates characteristic of the analogous monoradicals. We have recently shown by flash kinetics that the same conclusion holds for bimolecular trapping reactions.[7]

Results

Syntheses of Starting Ketones. Both α-AB and γ-CB were prepared by straightforward techniques: α-AB by reacting a butyrophenone iminate with allyl bromide;[8] γ-CB by addition of cyclopropyllithium to trimethylene oxide, conversion of the resulting alcohol to bromide, and Grignard addition to benzonitrile.

Photoproducts from α-AB. A degassed benzene solution 0.1 M in α-AB was irradiated at 313 nm. Gas chromatographic (GC) analysis showed six product peaks. The smallest peak had the same retention time as authentic 2-phenyl-2-norbornanol. A 16-g sample of α-AB in *tert*-butyl alcohol was irradiated under nitrogen with a Pyrex-filtered mercury arc in an immersion well to some 90% conversion. Five products were obtained by column chromatography on neutral alumina. The first three were purified by preparative GC and were assigned the followed structures: (1) 1-phenyl-4-penten-1-one (**5**) (by comparison to independently synthesized material), (2) 4-phenyl-3-ethyl-4-pentenol, and (3) 1-phenyl-2-allylcyclobutanol (**6**) (the latter two from their spectroscopic characteristics). The fourth product was shown to be 2-phenyl-2-norbornanol (**7**) by GC-MS. The fifth product was further purified by chromatography on silica gel and was identified as 3-phenyl-4-ethyl-3-cyclopentenol by its spectroscopic properties.

The five products isolated correspond to the last five of the six GC product peaks. The first was never isolated pure. A small sample was collected by GC and shown to be another unsaturated alcohol. No GC peaks were detected corresponding to 3-methyl-1-benzoylcyclopentane.

Photoproducts from γ-CB. Degassed benzene solutions 0.06 M in γ-CB were irradiated at 313 nm. GC analysis indicated only three major products. These were collected by preparative GC. Besides acetophenone, 1-phenyl-4-hepten-1-one (**8**) and 1-phenyl-4-cycloheptenol (**9**) were identified by their spectroscopic properties. The cis/trans ratio of **8** was not determined. There were also two minor products formed which were not identified. One eluted just before **8**. The other eluted just before the reactant ketone, where the expected cyclobutanol typically elutes.

Quantum Efficiencies. Degassed benzene solutions 0.1 M in α-AB or 0.06 M in γ-CB were irradiated at 313 nm in parallel with either benzophenone–pentadiene[9] or valerophenone[10] actinometers. Product yields were determined by GC analysis relative to known concentrations of alkane internal standards; quantum yields are listed in Schemes I and II. Addition of *tert*-butyl alcohol had only a small effect on quantum yields for γ-CB. For α-AB, the overall quantum efficiency was so low that no disappearance quantum yield was measured. For γ-AB, the disappearance quantum yield at 15% conversion was 0.43 in benzene and 0.42 in a 50:50 benzene–*tert*-butyl alcohol mixture. The

Scheme II

C$_6$H$_6$ (0.125)
50% *t*-BuOH (0.14)

8 (0.26)
(0.16)

9 (0.03)
(0.10)
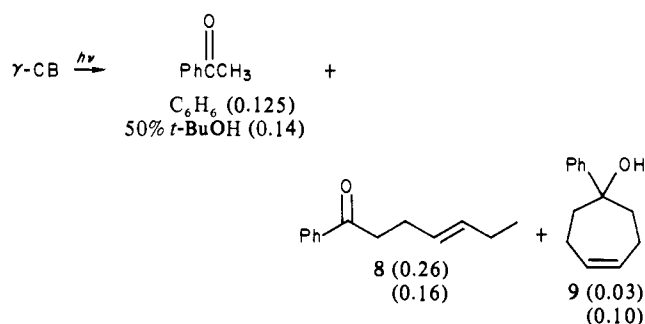
Scheme III
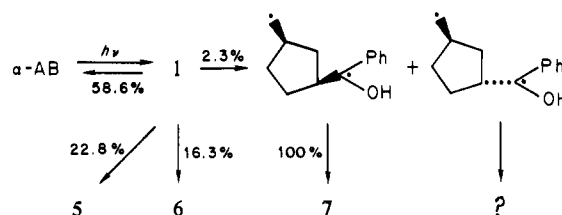
combined yields of products correspond to >95% material balance.

Quenching Studies. Degassed benzene solutions 0.1 M in α-AB or 0.045 M in γ-CB and containing various concentrations of 1,3-pentadiene were irradiated in parallel at 313 nm. GC analysis provided relative product yields at different quencher concentrations. Stern–Volmer plots were linear to $\phi^0/\phi = 4$ for both ketones, with slopes ($k_q\tau$) of 6.2 M^{-1} for α-AB and 20 ± 2 M^{-1} for γ-CB. All products from α-AB were quenched with equal efficiency. For γ-CB, $k_q\tau$ was 22 M^{-1} for acetophenone formation and 18 M^{-1} for heptenophenone formation. With $k_q = 5 \times 10^9$ M^{-1} s^{-1},[11] $1/\tau = 8.1 \times 10^8$ s^{-1} for triplet α-AB and 2.5×10^8 s^{-1} for triplet γ-CB.

Intersystem Crossing Yield of α-AB. Degassed benzene solutions 0.2 M in *cis*-1,3-pentadiene and 0.1 M in either α-AB or benzophenone were irradiated at 313 nm. The α-AB was 52.5% as effective as benzophenone at photosensitizing the cis → trans isomerization of the diene. The above quenching experiments indicate that 0.2 M diene quenches only 55% of triplet α-AB. Therefore, the intersystem crossing yield of α-AB is 96% that of benzophenone, or within experimental error of unity.[9]

Discussion

Products from α-AB. Morrison[12] and others[13] have already shown that γ,δ-unsaturated ketones such as 1-phenyl-4-hexen-1-one[14] undergo internal photocycloaddition to yield bicyclic oxetanes. Although we did not isolate any of the oxetanes expected from α-AB, we did isolate unsaturated alcohols of types which can be formed readily from the initial photoproducts.[14] We suspect that the first eluting product is the more stable[12] [2.2.0] oxetane[15] which rearranges during GC collection.

Two characteristic Norrish type II products were also formed from α-AB together with a very small but measurable quantity of **7**. We conclude that the type II biradical **1** does undergo a small amount of cyclization to a cyclopentylmethyl structure, the cis form of which can close to **7**. In terms of the two normal type II reactions of α-AB, the comparable yields of cyclization and cleavage are exactly what has been observed for α-methyl-

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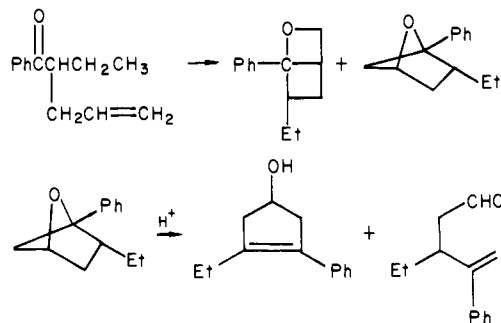
Scheme IV

butyrophenone (see Scheme III).[16]

The measured quantum yields for type II product formation allow an estimate of the type II 1,4-biradical lifetime. The ratio $(5 + 6)/7 = 24$. Lewis has reported that α-methylbutyrophenone undergoes type II reaction in 40% quantum efficiency.[16] If we assume a comparable 60% biradical disproportionation for α-AB, we conclude that biradical **1** cyclizes to **7** $^1/_{60}$th as rapidly as it undergoes normal reactions.

Beckwith has recently reported that the 3-propyl-5-hexen-1-yl radical, a close model for **1**, cyclizes with a rate constant of 5×10^5 s^{-1},[6] to form a 2.5/1 ratio of *cis*- and *trans*-3-propylcyclopentylmethyl radicals. Therefore, the monoradical rate constant for **1** → *cis*-**2** would be $\sim 3.6 \times 10^5$ s^{-1}. If the normal biradical reactions of **1** are 60 times faster than this, a normal biradical decay rate of 2.2×10^7 s^{-1} is indicated.

We note that we do not know the fate of the *trans*-**2** which must also be formed. We observed no 3-methyl-1-benzoylcyclopentane among the products, so *cis*-**2** apparently undergoes only coupling and no disproportionation. Our kinetics calculations assume that all *cis*-**2** formed cyclizes to **7**. We have already reported another example of a 1,5-hydroxy biradical in which disproportionation at OH is a minor reaction.[17]
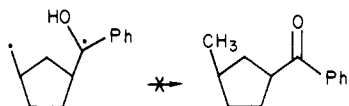
Triplet Kinetics of α-AB. The very low quantum yield for combined type II products from α-AB (0.0025) indicates that the major triplet reaction is interaction with the β-vinyl group.[14] The quenching studies indicate an overall triplet decay rate of 8×10^8 s^{-1}. Correction for the expected 60% biradical disproportionation to starting ketone[16] provides a total quantum yield for γ-hydrogen abstraction of 0.0063. Since $k_H = \phi/\tau$, $k_H = 5 \times 10^6$ s^{-1}, very similar to the value for unsubstituted butyrophenone,[18] as expected.

Given the known ability of alkenes to quench triplet ketones,[19] the rapid internal quenching by a β-vinyl group ($k \sim 8 \times 10^8$ s^{-1}) is not surprising.[20] The high intersystem crossing yield indicates negligible singlet quenching. We have already compared these results with Morrison's for β-propenyl ketones.[14] The most important conclusions are: (1) the rapid internal reaction between triplet carbonyl and double bond accounts for 99% of triplet decay but leads to bicyclic oxetanes with very low efficiency (1–2%); (2) since the β-propenyl group remains[19a] a faster quencher than the β-vinyl, this intramolecular quenching is not rotationally controlled.[21] We have already studied internal triplet ketone quenching by n donors (NR$_2$[22] and SR[23]) as a function of the number of methylenes between the two interacting groups. We are now studying a series of ω-unsaturated phenones to see how the distance dependence differs for a π donor.

Triplet Kinetics of γ-CB. The quenching studies indicate a triplet decay rate of 2.5×10^8 s^{-1}. The corresponding rate for the model γ-isopropylbutyrophenone (**10**) is 1.7×10^8 s^{-1} ($k_q\tau = 29$ M^{-1})[18] of which 1.6×10^8 s^{-1} corresponds to γ-hydrogen abstraction.[24] The faster decay rate for triplet γ-CB probably reflects a slight kinetic stabilization of the developing γ-radical site by the conjugated cyclopropyl group. The maximum value for this resonance enhancement factor[18] is 1.6. As discussed below, there may be a maximum of 24% of the triplet decay involving some direct interaction with the γ-cyclopropyl group. The corresponding rate constant for this unusual quenching process would be 6×10^7 s^{-1}, in which case the resonance enhancement factor would be only 1.2.

Products from γ-CB. The formation of both the heptenone **8** and the cycloheptenol **9** indicate that the 1,4-biradical **3** generated from triplet γ-CB undergoes the expected rearrangement to the 1,7-biradical **4**. Such cyclopropylcarbinyl-to-allylcarbinyl rearrangements have been observed in biradicals photogenerated from cyclic ketones[25] and from ketones and vinylcyclopropanes,[26] although they have never been used to estimate biradical lifetimes.

We can manipulate the results in two different ways in order to calculate the percentage of biradical rearrangement. The first involves comparison with the model γ-isopropylbutyrophenone (**10**). We assume that the 1,4-biradicals formed by γ-hydrogen abstraction in **10** and γ-CB would behave identically, except for the ability of the latter to rearrange. The photochemistry of **10** in benzene has been carefully studied;[18] it leads to acetophenone and a cyclobutanol in quantum efficiencies of 0.25 and 0.075, respectively. Since γ-CB forms acetophenone in only half the efficiency of **10**, we can conclude that biradical **3** undergoes 50% rearrangement. This conclusion presumes that there is no direct intramolecular quenching of the triplet carbonyl by the cyclopropyl group. To the extent that any such quenching occurs, the percentage rearrangement would be less than 50%.

Actually triplet **10** undergoes some 6% δ-hydrogen abstraction[24] which probably does not happen in triplet γ-CB (its δ-hydrogen is cyclopropyl). The appropriate correction in comparing acetophenone quantum yields suggests 53% rearrangement of biradical **3**.

The alternative method is to compare corrected product yields as we did for γ-AB. In fact, the two rearrangement products **8** and **9** are formed in twice the yield of acetophenone. Since **10** forms 30% as much cyclobutanol as acetophenone,[27] we conclude a total type II quantum yield of 0.16 for γ-CB, even though we could not analyze the cyclobutanol. Moreover, 65% of the biradicals revert to reactant, so that the 0.16 becomes 0.47. Heptenone **8** and cycloheptenol **9** represent disproportionation and

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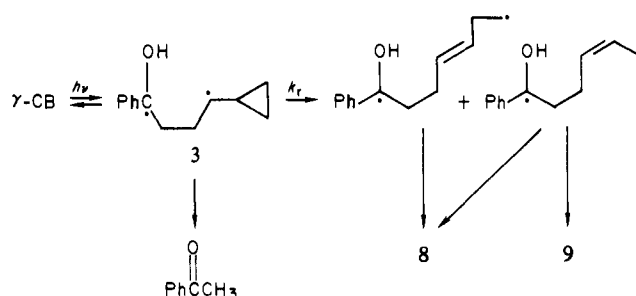(20) Cowan, D.; Baum, A. A. *J. Am. Chem. Soc.* **1970**, *92*, 2153.
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cyclization, respectively, the only two *expected* reactions of the 1,7-biradical **4**. The 0.29 combined quantum yield indicates a minimum rearrangement yield of 38% for biradical **3**. The problem is that some 24% of triplet γ-CB remains unaccounted for. The situation is even worse in 50% alcohol, where only 43% of triplet γ-CB gives products.

One possibility is that there is a direct quenching interaction, presumably charge transfer in character, between the γ-cyclopropyl group and the triplet carbonyl. Turro has reported some such phenomenon in α-cyclopropoxyacetophenones, with apparent rate constants $>10^8$ s^{-1}.[28] We do not know whether a γ-cyclopropyl group could quench at the high apparent rate of 6×10^7 s^{-1}. Alternatively, one might invoke unexpected reactions of biradical **4**. The high material balance speaks against this possibility. The low product efficiencies in 50% alcohol solvent also suggest some direct triplet quenching competitive with γ-hydrogen abstraction, since the latter is known to be slowed somewhat by alcohol solvents.[29]

Accordingly, we conclude that biradical **3** undergoes 38–53% rearrangement, probably closer to the lower figure. The value of $k_r\tau_3$ (see Scheme IV) is then 1.6–1.0. Beckwith has reported a rate constant of 2×10^7 s^{-1} for rearrangement of the model 1-cyclopropylethyl radical.[6] If **3** rearranges with the same rate constant, it then undergoes type II decay processes with a rate constant of 2–3 $\times 10^7$ s^{-1}.

Since 1,7-biradicals have not received much study, we should note some additional features of γ-CB photochemistry. The model 1-cyclopropylethyl radical opens to a 2.3 trans/cis ratio of 2-penten-5-yl.[6] Trans is also favored over cis in photoproduct yields.[25b] Therefore, we would expect a comparable predominance of *trans*-**4** over *cis*-**4**. Unfortunately, we cannot judge the relative ability of the two isomers to cyclize (to **9**) and to disproportionate (to **8**). The favored *trans*-**4** would do both slower than *cis*-**4** and may not even form *trans*-**9**. We observed that added alcohol increases the **9**/**8** ratio, having the usual[30] effect of retarding biradical disproportionation. The effect is only partial, unlike the situation with 1,4-biradicals but like the situation with 1,5-biradicals.[17] Presumably **4** goes predominantly to the enol form of **8**.
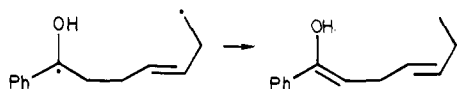

Biradical Lifetimes. Both α-AB and γ-CB undergo photorearrangements competitive with their type II reactions in amounts which indicate that their 1,4-biradicals undergo "normal" type II decay in 35–50 ns in benzene, if their rearrangement rates are the same as those for monoradicals. Scaiano has reported that the 1,4-biradicals formed from several different phenyl ketones all have lifetimes in benzene of 35–40 ns.[31] Since our lifetime range so closely overlaps Scaiano's measured[31] values, we can safely conclude that 1,4-biradicals indeed undergo radical rearrangements at rates negligibly perturbed from those for analogous model radicals.

It is important to emphasize that the measured biradical lifetime is independent of the exact mechanism for biradical decay, since the initial triplet 1,4-biradical can rearrange to another triplet biradical with no spin restrictions. Therefore, our experiments provide no evidence on the fundamental question whether the 35–50 ns measures the time required for triplet → singlet spin inversion in the 1,4-biradical or for chemical reaction of spin-equilibrated biradicals (~50:50 singlet:triplet). There certainly is strong evidence for spin correlation effects in hydrocarbon

biradicals such as trimethylene,[32] tetramethylene,[33] and trimethylenemethane.[34]

Scaiano has interpreted the small effects of substituents,[31] solvents,[5] and temperature[31] on type II 1,4-biradical lifetimes as indicative of a rate-determining spin flip for biradical decay. At the extreme, this mechanism would require rate constants well over 10^8 s^{-1} for chemical reaction of the singlet biradicals. Such rate constants are barely within the range allowed by the wide variations which have been observed in the rates of competing biradical reactions. Cyclization/elimination ratios in type II reactions of phenyl ketones vary from <0.1 to >100 depending on ketone and biradical structure.[16,27,35] This variation indicates a $\Delta\Delta G^*$ value of at least 5 kcal/mol for the competing biradical reactions. Such a large variation in ΔG^* values suggests that the largest ΔG^* value is at least 5 kcal, particularly since all the biradical reactions must have a negative ΔS^*.[3,16,27] Therefore, the variation in product ratios limits the singlet biradical decay rate constant to no more than 10^9 s^{-1}. In fact, Benson has derived Arrhenius parameters for cyclization and cleavage of singlet tetramethylene which extrapolate to a decay rate near 10^7 s^{-1} at 25 °C.[36]

Unfortunately, the type II biradicals whose lifetimes have been measured so far show very little variation in product ratios. Therefore, there is no reason to expect significant differences in biradical lifetimes whichever decay mechanism determines lifetimes. We are now attempting to measure biradical lifetimes for ketones which preferentially cyclize rather than cleave.[37] Meanwhile, we can point out that spin–orbit coupling may well be stronger and spin relaxation faster in type II biradicals than in pure hydrocarbon biradicals since there is considerable spin density on oxygen in α-hydroxy radical sites.[38] Therefore, spin inversion and chemical reactions of these 1,4-biradicals may occur at similar enough rates that lifetimes are determined partially by both types of processes.
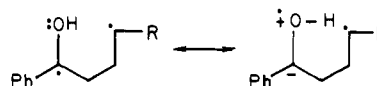
Experimental Section

Preparation of α-Allylbutyrophenone (α-AB). This ketone was prepared by the Stork–Dowd procedure.[8] The cyclohexylimine of butyrophenone (16 g, 0.068 mol) was added to 1.1 equiv of ethylmagnesium bromide in THF and then refluxed 1 h. To the room-temperature solution was added 9.1 g of allyl bromide (0.077 mol). This mixture was refluxed 18 h. The cooled solution was added slowly to 70 mL of 10% HCl and then refluxed 3 h. The cooled hydrolysis product was extracted into ether, washed with saturated sodium bicarbonate, and dried over MgSO$_4$. The ketone was purified as a colorless liquid by spinning-band distillation, bp 93 °C (0.6 Torr): IR (film) 3070, 3060, 2870, 1685, 1650, 1010, 920 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.9 (t, 3 H, $J = 8$ Hz), 1.3–2.0 (m, 2 H), 2.1–2.8 (m, 2 H), 3.45 (quintet, 1 H, $J = 6$ Hz), 4.8–5.1 (m, 2 H), 5.45–6.15 (m, 1 H), 7.3–7.5 (m, 3 H), 7.85–8.05 (m, 2 H); MS *m/e* 188 (M$^+$), 160, 105, 77.

Preparation of γ-Cyclopropylbutyrophenone (γ-CB). 3-Cyclopropyl-1-propanol was prepared by addition of an alkyllithium to trimethylene oxide.[39] Aldrich cyclopropyl bromide (13.2 g, 0.11 mol) in 20 mL of ether was added dropwise over 20 min to a vigorously stirred suspension of 1.20 g of lithium shot[40] in 20 mL of ether under an argon atmosphere. The resulting brown suspension of cyclopropyllithium and lithium bromide was refluxed an additional 10 min and was then cooled in an ice bath. A solution of 3.7 g of Aldrich trimethylene oxide (0.064 mol) in 10 mL of ether was added dropwise over 5 min. The resulting solution was

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allowed to stand at room temperature for 10 min and was then refluxed for 1 h. After 80 mL of benzene was added, the ether was distilled off and the solution was refluxed for 3.5 h. The cooled solution was treated with saturated aqueous ammonium chloride. The resulting aqueous layer was extracted once with ether. The combined benzene and ether solution was dried; distillation yielded 5.1 g (80% based on oxetane) of 3-cyclopropyl-1-propanol, bp 76 °C (17 Torr).

The alcohol was converted to the tosylate by treatment with tosyl chloride in pyridine at 0 °C for 24 h. The tosylate was separated by aqueous workup and ether extraction. The dry tosylate was added to 5.2 g of lithium bromide (freshly dried) in 60 mL of THF; the solution was kept at 25 °C for 2 h, 40 °C for 10 h, and refluxed for 2 h. The cooled mixture was poured into water and extracted with ether. Distillation afforded a 2.9 g of 3-cyclopropyl-1-bromopropane (59%), bp 89–90 °C (40 Torr).

The bromide was converted to the Grignard reagent in ether and was added to benzonitrile, following standard procedures,[41] to yield 1.5 g (45%) of crude γ-cyclopropylbutyrophenone. Pure ketone was collected by preparative GC: IR (CCl$_4$) 3070, 1685, 1595, 1495, 1015 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.2–0.8 (m, 4 H), 1.0–1.2 (m, 1 H), 1.2–1.45 (m, 4 H), 1.6–2.1 (m, 2 H), 2.94 (t, 2 H, J = 7.5 Hz), 7.1–7.4 (m, 3 H), 7.7–7.9 (m, 2 H); MS m/e 188 (M$^+$), 120 (base), 105, 77.

Preparation of 3-Methyl-1-benzoylcyclopentane. PBr$_3$ (11 g) was added dropwise over 40 min to 12 g of Aldrich 3-methylcyclopentanol at room temperature. The reaction mixture was stirred for 3 days. It was then poured into ice–water. The organic phase was separated, washed with dilute Na$_2$CO$_3$, and dried over Na$_2$CO$_3$. Vacuum distillation (15 Torr) provided 15 g of mixed cis- and trans-3-bromo-1-methylcyclopentane. This was converted to the Grignard reagent in ether and reacted with 20 g of benzonitrile as usual.[41] After workup, 12 g of a mixture of the two isomeric ketones was obtained.

Other Chemicals. Benzene was purified by treatment with sulfuric acid and distillation from P$_2$O$_5$. Aldrich 1,3-pentadiene (mixed isomers) was used as quencher. Long-chain alkanes as internal standards were available from previous work in these laboratories as was valerophenone. Chemical Samples Co. cis-1,3-pentadiene was used as received.

General Procedures. Generally, samples were irradiated in 13 × 100 mm Pyrex tubes which had previously been degassed and sealed. Sample tubes were always irradiated in parallel with valerophenone actinometers[10] on a rotating "merry-go-round".[42] The 313-nm region of a 450-W Hanovia medium-pressure mercury arc was isolated with an alkaline chromate filter solution.[10] Product and reactant concentrations were determined by GC analysis with FID detectors. Pentadiene isomerization was monitored at 50 °C on a 25-ft column containing 25% 1,2,3-tris(2-cyanoethoxy)propane on Chromosorb P. α-AB products were analyzed at 140 °C on an 8-ft column containing 4% QF-1 and 1% Carbowax 20M on Chromosorb G. γ-CB products were analyzed at 150 °C on an identical column only 6 ft long. Acetophenone formation was monitored at 130 °C. Varian 600 and 1200 gas chromatographs were used with an Infatronics digital integrator. NMR spectra were recorded on Varian T-60 and HA-100 spectrometers; mass spectra on a Perkin-Elmer Hitachi RU-6.

Identification of Photoproducts from γ-Cyclopropylbutyrophenone. Degassed benzene solutions 0.06 M in ketone were irradiated at 313 nm in 5-mL tubes for 44 h. The combined solutions were analyzed by GC. At low conversion there were only three major product peaks; the corresponding products were collected by preparative GC on a 0.25-in. column. The most volatile was acetophenone. A product 8 eluted 7 min before reactant ketone; product 9, 8 min later, both at 140 °C column temperature. Two small product peaks eluted just before and after 8. These were not identified.

Product 8 was identified as 1-phenyl-4-hepten-1-one on the basis of the following information: MS m/e 188 (M$^+$), 120, 105 (base), 77; IR (CCl$_4$) 3020, 2870, 1685, 965, 900, 730, 695 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.9 (t, 3 H, J = 7 Hz), 1.8–2.1 (m, 2 H), 2.2–2.6 (m, 2 H), 2.95 (t, 2 H, J = 7 Hz), 5.4 (m, 2 H), 7.1–7.4 (m, 3 H), 7.65–7.85 (m, 2 H). The IR peaks at 965 and 695 cm^{-1} together with an apparent 2-Hz splitting of the NMR resonance at δ 2.95 suggest the presence of both cis and trans isomers. A sample of 1-phenyl-1-heptanone had an almost identical GC retention time as 8.

Product 9 was identified as 1-phenyl-4-cycloheptenol on the basis of the following information: MS m/e 188 (M$^+$), 170, 91; IR (CCl$_4$) 3400 (br), 3060, 3040, 3000, 1595, 1490, 1445, 1060 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.5 (s, 1 H), 1.6–2.8 (m, 8 H), 5.75 (m, 2 H), 7.0–7.45 (m, 5 H). A sample of 1-phenylcycloheptanol had the same GC retention time as 9.

Identification of Photoproducts from α-Allylbutyrophenone. The ketone (16 g) in 180 mL of tert-butyl alcohol was irradiated under nitrogen in an immersion well with a Pyrex-filtered 450-W Hanovia mercury arc until less than 10% of starting ketone remained. GC analysis showed six products, none of which had the retention time of 3-methyl-1-benzoylcyclopentane. The solvent was stripped off and the residue was chromatographed on neutral alumina with 50:50 cyclohexane:chloroform as eluent. Five separate products were isolated. The first three were further purified by GC through a column packed with 15% QF-1 and 3% Carbowax 20M.

The first was assigned as 1-phenyl-4-penten-1-one by comparison of its spectroscopic characteristics with those of the independently prepared compound (Grignard addition of 4-bromo-1-butene to benzonitrile): IR (neat) 3085, 3075, 1685, 1625, 1440, 1200, 920 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.50 (pseudo-quartet, 2 H, J = 6.5 Hz), 3.00 (t, 2 H, J = 6.5 Hz), 4.9–5.2 (m, 2 H) 5.5–6.2 (m, 1 H), 7.3–7.5 (m, 3 H), 7.8–8.0 (m, 2 H); MS m/e 146, 105, 77.

The second eluted product was assigned as 4-phenyl-3-ethyl-4-pentenal on the basis of the following properties: IR (neat) 3080, 3060, 3025, 2810, 2710, 1730, 1630, 1520, 910 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.90 (t, 3 H, J = 6.5 Hz), 1.55 (quintet, 2 H, J = 6.5 Hz), 2.58 (d of d, 2 H, J = 6.5, 1.1 Hz), 3.16 (quintet, 1 H, J = 6.5 Hz), 5.1 (s, 1 H), 5.35 (s, 1 H), 5.90 (br s, 5 H), 9.8 (t, 1 H, J = 1.3 Hz); MS m/e 188, 144.

The third eluted product was assigned as 1-phenyl-2-allylcyclobutanol: IR (neat) 3540, 3410 (br), 3060, 3020, 1640, 1495, 1450, 925 cm^{-1}; ^{1}H NMR (CDCl$_3$) 1.1–2.9 (m, ~8 H), 4.93–5.16 (m, 2 H), 5.5–6.15 (m, 1 H), 7.35 (br s, 5 H); MS m/e 188, 170.

A fraction containing 70% of the fourth product was analyzed by GC–MS. Its MS was identical with that of an authentic sample of 2-phenylbicyclo[2.2.1]heptanol-2, provided by B. Lam and Professor D. Farnum: m/e 188, 170, 142, 115. The MS of the authentic sample was quite different when injected directly than when injected via GC, there being more dehydration by the latter procedure.

The last eluting product was purified by separate chromatography on silica gel with benzene as eluent. It was assigned as 3-phenyl-4-ethyl-3-cyclopentenol: IR (neat) 3620, 3450 (br), 3080, 3060, 3030, 1610, 1500, 1190, 1075, 1025 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.02 (t, 3 H, CH$_3$, J = 7 Hz), 2.1–3.5 (complex m, 6 H), 4.50 (m, 1 H, H$_g$), 7.30 (br s, 5 H, Ph). Addition of a twofold molar excess of Eu(fod)$_3$ resulted in the following 100-MHz ^{1}H NMR: δ 1.4 (t, J$_{AB}$ = 7.5 Hz, CH$_2$CH$_3$), 2.9 (quartet, J = 7.5 Hz, CH$_2$CH$_3$), 4.04 (dd, H$_c$, J$_{ce}$ = 17 Hz, J$_{cg}$ = 6 Hz), 4.39 (dd, H$_d$, J$_{df}$ = 17 Hz, J$_{dg}$ = 6 Hz), 5.55 (d, H$_e$, J$_{ce}$ = 17 Hz), 5.91 (d, H$_f$, J$_{df}$ = 17 Hz), 7.02–7.9 (complex m, Ph), 9.0 (t, H$_g$, J$_{cg}$ ~ J$_{dg}$ =
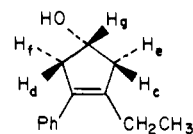
6 Hz). In decoupling experiments, irradiation at δ 4.39 (H$_d$) caused the δ 5.91 doublet to collapse to a singlet.

Of the six GC detected products, the earliest eluting one was missed by column chromatography. A small sample was collected by preparative GC. NMR and IR analysis showed it to be an alcohol with a double bond but no vinyl protons and the ethyl group intact.

Quantitative Studies. Solutions 0.1 M in α-AB and 0.0092 M in n-tetradecane (internal standard) were irradiated for 50 h, which led to 8.6% maximum conversion. Total light intensity was measured by irradiating aliquots of identical 0.1 M benzophenone–0.4 M cis-pentadiene samples for 8–10-h intervals throughout the 50 h. Relative responses of 5, α-AB, and standard were determined from weighed mixtures. Responses of isomeric photoproducts were assumed equal to that of α-AB. Hexadecane was the internal standard for measuring acetophenone formation from valerophenone. γ-CB was studied as 0.05 M solutions containing 0.0045 M n-heptadecane as internal standard. They were irradiated 2.5 h which led to 14% maximum conversion. Again, GC responses of isomeric photoproducts were assumed equal to that of γ-CB.

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