

Photochemistry of δ -Halo Ketones: Anchimeric Assistance in Triplet-State γ -Hydrogen Abstraction and β -Elimination of Halogen Atoms from the Resulting Diradicals

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Abstract: UV irradiation of δ -chloro-, bromo-, and iodovalerophenones forms 4-benzoyl-1-butene as well as acetophenone. Comparable elimination of HX does not occur with γ -halo ketones but does to some extent with ϵ -iodohexanophenone. This elimination of HX is shown to proceed from the diradical formed by triplet state γ - (or δ -) hydrogen abstraction; it represents typical radical β -cleavage competing with normal diradical decay. As expected, the rate constant for this monoradical diradical reaction increases in the order $\text{Cl} < \text{Br} < \text{I}$, with k_{-X} for Cl being $4 \times 10^6 \text{ s}^{-1}$, for Br $\geq 3 \times 10^8 \text{ s}^{-1}$, and for I $> 5 \times 10^9 \text{ s}^{-1}$. Highly efficient photoelimination of HCl and HBr from 4-halo-1,4-dimethyl-1-benzoylcyclohexanes demonstrates that elimination of $X\cdot$ from the diradical does not involve a cooperative interaction between both radical sites. Small solvent and substituent effects on product ratios rule out any significant zwitterionic contribution to the elimination transition state. The rate of triplet γ -halogen abstraction in the δ -halo ketones also increases in the order $\text{Cl} < \text{Br} < \text{I}$ ($k_{\text{I}}/k_{\text{Cl}} = 7.7$), with the rate for the δ -iodo ketone being faster than for valerophenone itself. In the 4-bromo-1-benzoylcyclohexanes, the diastereomer with axial bromine undergoes triplet δ -hydrogen abstraction six times faster than the diastereomer with bromine equatorial. All three facts indicate substantial "anchimeric assistance" to δ -hydrogen abstraction similar to that previously observed for bimolecular reactions of Br atoms. It is suggested that maximum quantum yields for γ, δ -elimination ~ 0.5 indicate a heavy-atom-induced $T \rightarrow S$ radiationless decay during γ -hydrogen abstraction. It is further noted that the high chemical yield of 4-benzoyl-1-butene demands an unusually efficient in-cage reaction of a triplet ketyl-halogen radical pair. Especially rapid intersystem crossing and electron transfer in such a radical pair are quite plausible.

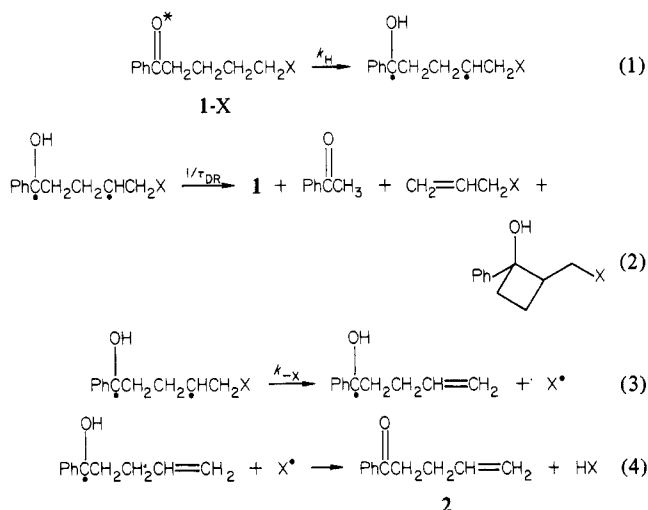
Introduction

Several years ago we established that the 1,4-diradical intermediates which intervene in Norrish type II photoreactions^{1,2} undergo bimolecular trapping³ and typical free-radical rearrangements.⁴ More recently we have shown that these monoradical reactions of the diradicals proceed with the same rate constants which characterize the reactions of analogous monoradicals.^{5,6} This conclusion was facilitated by Scaiano's elegant direct flash spectroscopic determinations of diradical lifetimes.^{7,8} Since we now know diradical lifetimes, we can synthesize ketones substituted such that previously unmeasured rate constants for other free-radical reactions might be determined by the competitive reactions of the ketone-derived diradicals.

The first radical reaction we have investigated is β -cleavage, which can be monitored by the photochemistry of δ -substituted ketones. The highly regioselective γ -hydrogen abstraction characteristic of triplet ketones⁹ allows the transient generation of diradicals with a wide variety of substituents β to the γ radical site of the diradical. Scheme I demonstrates the important reactions, reaction 2 including all normal 1,4-diradical reactions and reaction 3 being the anticipated "monoradical" reaction of the diradical.

We have already communicated the fact that reactions 3 and 4 do occur with δ -halo and δ -sulfur substituents and simultaneously reported the only extensive list of radical β -cleavage rate constants.¹⁰ In this paper we report in full our results for δ -halo

Scheme I



ketones. We shall report the results for other δ -substituted ketones separately, primarily because of appreciable differences in the excited-state chemistry of the various types of substituted ketones. Moreover, the intense interest in the properties of β -halo radicals^{11,12} warrants special attention.

Results

δ -Halovalerophenones. δ -Chloro-, -bromo-, and -iodovalerophenone, (1-Cl, 1-Br, and 1-I, respectively) were prepared and purified by standard procedures. Dilute benzene solutions of the three ketones were irradiated at 313 nm. We had noted previously that 1-Cl undergoes a minor reaction in competition with type II elimination.¹³ In fact, 4-benzoyl-1-butene (2) is a minor

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Table I. Photokinetic Data for δ -Halovalerophenones^a

ketone	Φ_{II}^b	Φ_2	Φ_K	$k_q\tau, M^{-1}c$	$1/\tau, 10^7 s^{-1}d$
1-Cl	0.62 ± 0.03^e	0.10 ± 0.01	0.82 ± 0.05	230 ± 10^f	2.2
1-Br	0.048 ± 0.003	0.55 ± 0.03	0.60 ± 0.03	90 ± 5	5.6
1-I	<0.002	0.43 ± 0.03		30 ± 3	16.7

^a Degassed benzene solutions containing 0.1 M ketone and 0.1 M pyridine irradiated at 313 or 366 nm, 25 °C. Average of duplicate runs recorded. ^b Acetophenone yield. ^c Naphthalene quencher, 366-nm irradiation. ^d $k_q = 5 \times 10^9 M^{-1} s^{-1}$. ^e The measured cyclobutanol yield is 0.08, ref 13. ^f Same as literature value, ref 13.

Table II. Effect of Solvent and Substituents on Product Quantum Yields from δ -Chlorovalerophenone^a

substituent	solvent	Φ_{II}	Φ_2
none	C ₆ H ₆	0.62	0.10
none	CH ₃ CN	0.54	0.08
none	CH ₃ OH	0.36	0.06
<i>p</i> -OCH ₃	C ₆ H ₆	0.045	0.008
<i>p</i> -CF ₃	C ₆ H ₆	0.63	0.07
	CH ₃ CN	0.63	0.04
	CH ₃ OH	0.43	0.03

^a Same conditions as Table I.

product from 1-Cl, with acetophenone the major product and a cyclobutanol the other type II product. The 1-Br solution turned yellow upon irradiation and yielded 2 as the major product. The 1-I solution turned red; 2 was the only volatile organic product.

The colored photosylates from 1-Br and 1-I suggested the formation of free bromine and iodine. When quantitative studies were attempted, the measured quantum yields for formation of 2 from 1-Br were erratic whereas the acetophenone yield was not. Since both HX and X₂ can add readily to 2, pyridine was added to the solution to trap the HX expected from reaction 4. The presence of 0.01 M pyridine was sufficient to maximize the low conversion yield of 2 at a value 1.5 to 2 times higher than those measured in the absence of base. Moreover, irradiated solutions of 1-Br and 1-I remained colorless and yielded white precipitates of pyridinium hydrohalide. That the pyridine did not undergo any dark reactions with halo ketone was established by noting no formation of either 2 or pyridinium salt in samples held in the dark for several days. Moreover, the presence of 0.1 M pyridine did not affect the NMR spectrum of 1-I in benzene even after several days.

All quantitative measurements were performed on solutions 0.1 M in ketone and 0.1 M in pyridine. The pyridine enhances type II yields¹⁴ besides trapping HX. Product quantum yields, disappearance yields, and triplet decay rates are listed in Table I. The latter were determined by standard Stern-Volmer quenching studies¹⁵ with various concentrations of naphthalene as quencher and with 365-nm irradiation. Quenching plots were linear in the presence of 0.1 M pyridine; the derived quenching constants were the same when monitoring either acetophenone or 2 and are listed in Table I. Lifetimes were determined on the basis that $k_q = 5 \times 10^9 M^{-1} s^{-1}$.¹⁶ Material balances for 1-Cl and 1-Br were $100 \pm 5\%$; decomposition of 1-I during analysis prevented measurement of a disappearance yield. (No 2 or acetophenone results from this thermal decomposition.)

Table II lists the minor variations observed in product yields from 1-Cl upon changing to more polar solvents and upon addition of ring substituents.

Scheme II

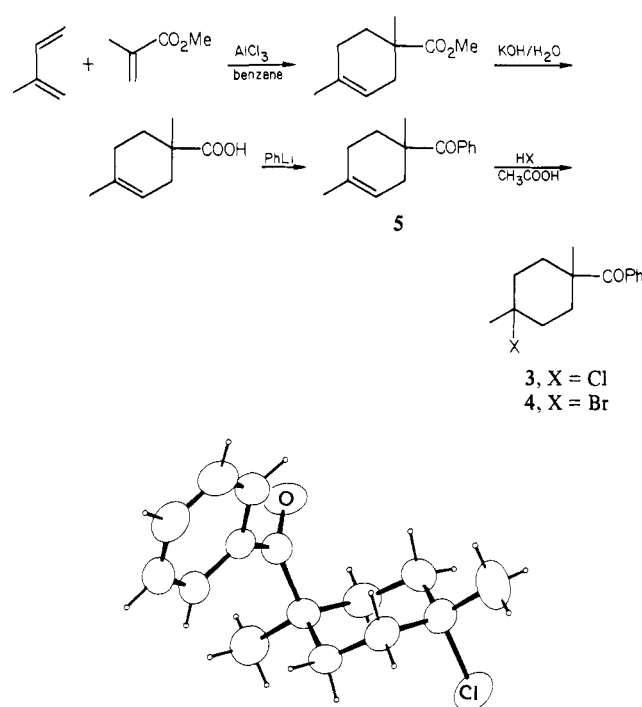


Figure 1. ORTEP⁵³ drawing of the molecular structure of *trans*-3. The thermal ellipsoids have been scaled to include 50% probability; the thermal parameters for H atoms have been set to an arbitrary small value.

All three ketones and valerophenone were equally efficient at sensitizing the *cis* \rightarrow *trans* isomerization of 1,3-pentadiene, as measured after 1% conversion of solutions 0.05 M in ketone, 0.1 M in pyridine, and 0.5 M in diene. Therefore, all three δ -halo-valerophenones have intersystem crossing yields of unity.¹⁷

UV spectra of the three ketones are virtually identical with that of valerophenone. The phosphorescence spectrum of 1-Cl is identical with that of valerophenone; those of 1-Br and 1-I are very similar, with the same 0,0 bands, but show one and two extra peaks, respectively, between the four of $\sim 1700\text{-cm}^{-1}$ spacing normally discernible for n, π^* emission of phenyl ketones.

No CIDNP phenomena could be observed during irradiation of 1-Br or 1-I solutions.

Control Experiments. Neither 1 M ethyl iodide nor 1 M butyl bromide measurably quenched the photoelimination of butyrophenone (0.1 M in benzene). Since butyrophenone has a triplet lifetime of some 130 ns,¹³ the maximum rate constant for bimolecular interaction between the alkyl halides and a triplet carbonyl group can be set as less than $5 \times 10^5 M^{-1} s^{-1}$.

The benzoylbutene 2 itself undergoes only very slow photodecomposition. In order to see whether photoelimination of HX is specific to δ -halo ketones, we irradiated 0.1 M benzene solutions of β -chloropropiophenone and γ -chloro- and γ -bromobutyrophenone for periods sufficient to produce at least 50% conversion in the δ -halo ketones. In no case was any benzoylalkene detected as product, although the latter two ketones produced acetophenone as expected.¹³ Irradiation of dilute ϵ -iodohexanophenone did produce some 5-benzoyl-1-pentene in one-tenth the yield of acetophenone.

Some 4-benzoyl-1-butyl tosylate was prepared. It unfortunately forms 2 during GC analysis. However, irradiation of a dilute benzene solution produced acetophenone with a quantum yield of 0.4.

4-Halo-1,4-dimethylbenzoylcyclohexanes. These compounds were prepared by addition of HCl or HBr to 1,4-dimethyl-4-benzoylcyclohexene (5), which was prepared by an $AlCl_3$ -catalyzed Diels-Alder addition of methyl methacrylate to isoprene, followed

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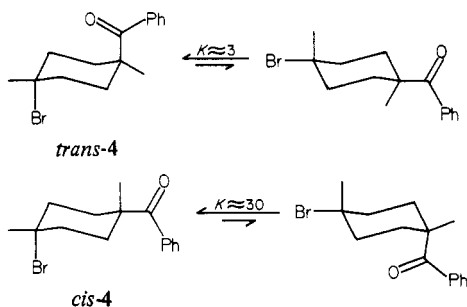
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Table III. Photokinetics Data for 4-Halo-1,4-dimethyl-1-benzoylcyclohexanes^a

ketone	Φ_I^b	$k_q\tau_I, M^{-1}$	Φ_s^c	$k_q\tau_s, M^{-1} c$	$10^7 s^{-1}$	
					$1/\tau_I$	$1/\tau_{II}$
<i>trans</i> -3	0.008	233 ± 20	0.21 ^d	100 ± 10	2.2	5.0
<i>trans</i> -4	0.018 ± 0.001	208 ± 15	0.42 ± 0.02	16.5 ± 4	2.4	30
<i>cis</i> -4	0.11	210 ± 10	0.08	65 ± 5	2.4	7.7
7 ^e	0.20	200	0.045	29	2.5	17

^a Same conditions as Table I except 0.05 M ketone, 0.05 M pyridine, and 0.02 M butanethiol. ^b Benzaldehyde formation. ^c Disappearance of 0.05–0.10 M pyridine. ^d $\Phi_6 = 0.01$. ^e All data from ref 19.

Scheme III



by hydrolysis of the cyclic ester and reaction of the acid with phenyllithium (Scheme II). The catalyzed Diels–Alder reaction proceeded regiospecifically, whereas the uncatalyzed thermal reaction produced a mixture of 3- and 4-carbomethoxycyclohexenes.

In the case of 4, the *cis* and *trans* diastereomers were separable by fractional crystallization. In the case of 3, only one isomer could be crystallized. X-ray analysis showed it to be *trans*-3, as shown in Figure 1.

The crystal structure of *trans*-3 corresponds to what would be expected to be the major conformation in solution. At C-4 there should be a $\sim 10/1$ preference for methyl equatorial,¹⁸ while at C-1 there should be a 3/1 preference for methyl axial.^{19,20} Scheme III depicts the expected conformational equilibria for *trans*- and *cis*-4. Note that the 1-methyl is predominantly axial in the *cis* isomer, equatorial in the *trans*.

Both ¹H and ¹³C NMR signals of axial methyl groups appear upfield relative to equatorial methyls.²¹ The ¹H NMR spectra of *cis*- and *trans*-4 are quite similar, the main difference being an 0.16-ppm difference in the upfield methyl signals corresponding to the 1-methyl groups (δ 1.32 and 1.43, respectively). The corresponding signal for *trans*-3 occurs at δ 1.40. (The 4-methyl signal for 3 appears 0.23 ppm upfield from that for *trans*-4, as expected.²²) A similar large difference occurs in the ¹³C NMR, the upfield methyls of *trans*-3 and *trans*-4 appearing at δ 27.5, that of *cis*-4 at δ 21.8.

The addition of Eu(fod)₃ allowed a more qualitative but striking differentiation between *cis*- and *trans*-4. Figure 2 depicts such shifted ¹H NMR spectra for all three compounds. The methylene signals for the two *trans* compounds are nearly identical, whereas those for *cis*-4 differ appreciably in positioning and splitting. Even without complete separation and resolution of the various peaks, the symmetries of the spectra allow stereochemical assignments.

Photochemistry of 4-Halo-1-benzoyl-1,4-dimethylcyclohexanes. GC analysis of both 3 and 4 under all conditions attempted resulted in thermal dehydrohalogenation, peaks for both 5 and parent ketone appearing. Analogous elimination occurred during column

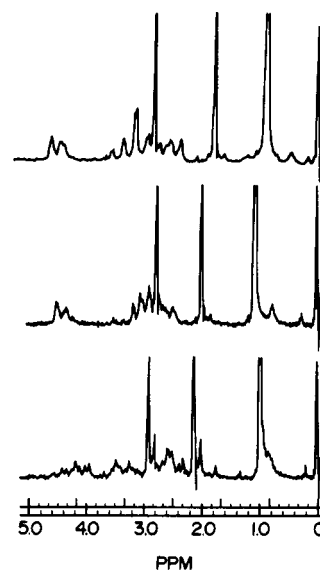
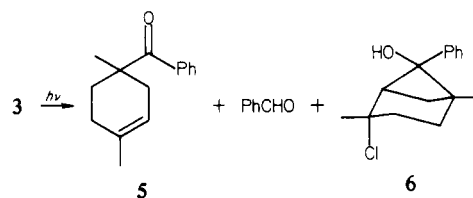


Figure 2. Eu(fod)₃-shifted ¹H NMR spectra of *trans*-3 (top), *trans*-4 (middle), and *cis*-4 (bottom).

chromatography. However, 3 did not decompose upon TLC analysis and the major photoproduct spot corresponded to 5. After sufficient irradiation that no GC peaks remained for 3 and 4, the major product was always 5 with variable amounts of benzaldehyde and, in the case of 3 a GC peak thought to represent the expected^{19,20} type II cyclization product 6. Unfortunately, this compound could not be isolated.



Indirect proof for the formation of 5 and 6 was obtained as follows. An IR spectrum of an irradiated solution of 3 showed a strong OH stretch at 3500 cm⁻¹. Addition of bromine to this crude photosylate resulted in the precipitation of the orange dibromo addition compound which was formed independently from authentic 5.

Product quantum yields are listed in Table III. The yield of 5 from 3 was measured directly when it was observed that GC analysis of unirradiated 3 produced a consistent amount of 5. Irradiated samples all produced extra 5. Since both isomers of 4 undergo extensive decomposition during analysis, their reactions were followed indirectly. Since the yield of HX should equal the yield of 5, the HX was trapped with pyridine. All quantitative data were obtained by irradiation of benzene solutions containing 0.05 M ketone, 0.05 M pyridine, and 0.02 M butanethiol. Previous work showed that the thiol traps all free benzoyl radicals as benzaldehyde.^{19,20,23} The disappearance of pyridine (20–40%) was measured by GC analysis and, in the case of 3, was shown

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(23) (a) Wagner, P. J.; McGrath, J. M. J. Am. Chem. Soc. 1972, 94, 3849. (b) Lewis, F. D.; Hilliard, T. A. Ibid. 1972, 94, 3852.

to equal the yield of **5**. Comparable equivalence of pyridine loss and **5** formation was assumed for **4**. As mentioned above, pyridinium hydrohalide salts precipitated from solution during irradiation. Quenching studies were performed with 1-methylnaphthalene quencher and 365-nm irradiation. For all three ketones, benzaldehyde formation was quenched far more readily than was formation of **5** or **6**. Table III lists quantum yield and lifetime data for all three ketones and includes comparable data for the model 1-methyl-1-benzoylcyclohexane (**7**).¹⁹

A final blank experiment verified that 0.5 M acetophenone does not photosensitize the dehydrobromination of 1 M 1-bromo-1-methylcyclohexane.

Discussion

Mechanism for $\gamma\delta$ -Elimination. No such remote photoinduced elimination had been observed before this work. Although n,π^* singlet aliphatic ketones can sensitive homolysis of alkyl halide bonds,²⁴ triplet phenyl ketones apparently do not. We found that triplet acetophenone does not sensitive dehydrohalogenation of several alkyl halides. Moreover, neither ethyl iodide nor butyl bromide quenches triplet ketones with rate constants as high as $10^6 \text{ M}^{-1} \text{ s}^{-1}$. Several independent studies have established that β and γ substituents on phenones are effectively $>1 \text{ M}$, while δ substituents are effectively $<1 \text{ M}$.²⁵ Therefore, the lack of photoelimination from β - and γ -halo ketones definitely establishes that the reaction of δ -halo ketones does not involve some sort of direct interaction between the triplet carbonyl and the C-X bond. The formation of **2** from the δ -halo ketones does not represent a general reaction between triplet ketones and alkyl halides. Rather the elimination seems to require the availability of a readily abstractable hydrogen atom β to the halogen.

The inductive effects of δ substituents on rates of γ -halogen abstraction are well understood and predictable.¹³ Any concerted triplet process leading to loss of HX would necessarily be reflected in a triplet decay rate greater than that expected for simple γ -hydrogen abstraction, since the rates for the latter would be expected to be very similar for 1-Cl, Br, I and must be unaffected by any competing reaction.²⁶ In fact, the rate of triplet decay does increase as the percentage of **2** formed increases. However, the >100 -fold change in product ratio is far greater than the eightfold increase in $1/\tau$. Even if there were some concerted reaction for 1-I, γ -hydrogen abstraction would still comprise over one-eighth the total triplet decay. The observation of no acetophenone means that *all* of the 1,4-diradicals undergo a competitive reaction involving loss of I. The same sort of reasoning indicates that *most* of the 1,4-diradicals formed from 1-Br must lose Br.

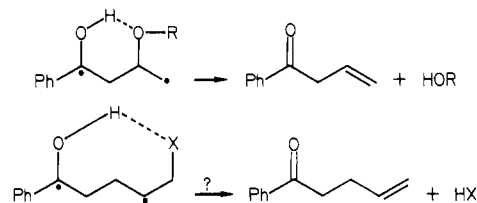
No concerted reaction from triplet **1** to triplet **2** plus H-X seems possible because dehydrohalogenation is endothermic. It is conceivable that the halogens could induce enough spin-orbit coupling to allow triplet **1** \rightarrow ground state **2**. However, the above considerations indicate the reaction involves primarily interaction of the triplet carbonyl with a γ hydrogen rather than with a δ halogen. A synchronous γ -hydrogen abstraction and δ -X cleavage can be visualized. However, such clearly does not occur during other free-radical abstractions of hydrogen β to halogen.¹¹ Therefore, the most rational mechanism for the observed loss of HX is precisely that shown earlier in Scheme I, β -cleavage of X- from a 1,4-diradical.

The ability of ϵ -iodohexanophenone to undergo some photoinduced loss of HI is consistent with some competitive δ -hydrogen abstraction. Normally the γ/δ hydrogen abstraction ratio is $\sim 15/1$.⁹ The ϵ iodine would be expected to deactivate the γ carbon by 50%¹³ so the observed 10/1 product ratio does not demand any new mechanism for loss of HI.

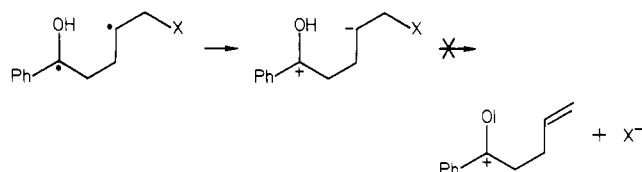
Nature of Halogen Atom Cleavage. We have used the rate constant k_{-X} in reaction 3. We must now ask whether its value is the same as would obtain for an analogous monoradical or

whether the second unpaired electron of the diradical can affect the process. In other papers^{5,6} we conclude that monoradical reactions of such diradicals proceed with normal rate constants. Therefore, we can assign the k_{-X} values for the diradicals as those characteristic of radicals in general, provided that no special diradical mechanism for cleavage exists. In fact, two such mechanisms involving both free electrons seem possible.

We reported several years ago that β -alkoxy ketones undergo 1,2-elimination of alcohol via the type II 1,4-diradical and suggested a six-atom cyclic transition state.²⁷ A comparable process here would require an eight-atom cycle and seemed less likely. The highly efficient photoelimination from **3** and **4**, where the X and OH are too far apart for any cyclic process, demonstrates that a concerted diradical reaction does not contribute significantly to overall elimination.



Another two-electron mechanism for diradical elimination would be loss of an anion from a zwitterionic form of the singlet diradical.



The data in Table II make this possibility very unlikely. Neither ring substituents nor solvent polarity significantly alter the product ratio from 1-Cl. If k_{-X} measured formation of an ion pair, polar solvents and a *p*-methoxy substituent would certainly have increased the relative yield of **2**. Although the CF_3 group slightly decreases the yield of **2**, solvent effects on this compound do not support an ionic mechanism. The tosylate group would be expected to be at least as good an anionic leaving group as Br, yet unlike 1-Br δ -tosyloxyvalerophenone undergoes type II elimination in high quantum efficiency.

We are thus left with a simple monoradical cleavage, unaffected by the other unpaired electron, as the remaining plausible mechanism for loss of X- from the 1,4-diradical.

Formation of HX. All the mechanistic considerations point to the formation of a ketyl-halogen radical pair as shown in reaction 3. This radical pair presumably is formed as a triplet, since the diradical is so formed.^{2,8} The 100% material balances together with the absence of detectable Br_2 or I_2 (in the presence of pyridine) demand that few of the initially formed pairs diffuse apart. This is a most unusual conclusion. It is worth reiterating that the kinetics demand that at least half the elimination of 1-Br involves the 1,4-diradical. We must therefore consider the likelihood of reaction 4 being a highly efficient in-cage reaction. The fact that one of the free spins resides entirely on a halogen could well promote so much spin-orbit coupling that singlet \leftrightarrow triplet interconversion of the radical pair would be faster than usual. Any subsequent radical-radical reaction of the pair would lead to **2** and HX. The high electron affinity of halogen atoms and the low oxidation potential of ketyl radicals²⁸ combine to suggest that electron transfer would be very rapid, even in benzene. Disproportionation in fact is a redox reaction in this case. Scaiano has reported rate constants greater than $10^9 \text{ M}^{-1} \text{ s}^{-1}$ for oxidation of ketyl radicals by several large organic oxidants.²⁸ The necessary orbital overlap with a halogen atom should be much better. Therefore, both requisites for efficient in-cage reaction are satisfied

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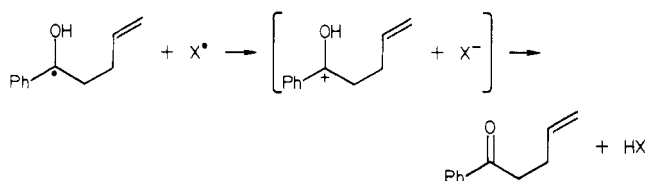
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in this case, the redox-disproportionation having precedent in Kropp's work on the photochemistry of alkyl halides, where less readily oxidized alkyl radicals are involved.²⁹ It should be noted that reaction 4 probably leads to both keto and enol tautomers of **2**.³⁰



The apparent high efficiency of reaction 4 strongly suggests that reaction 3 is effectively irreversible. Certainly the addition of atomic Br or I to an alkene could not be fast enough to compete with a radical-radical reaction. Reactions of atomic Cl with alkenes are very rapid; nonetheless the proposed in-cage redox reaction should have essentially zero free energy of activation and should dominate any simple radical addition.

Values of k_{-X} . The product ratios give the following order of relative rate constants: Cl/Br/I = 1/70/>1300. The only assumption involved is that the normal type II reactions of the diradicals occur in the same proportion for all three. This relative ordering of cleavage propensities is what would be expected from known bond energies. Actual k_{-X} values can also be derived from the results and bear more discussion.

The chemistry of 1-Cl has been studied the most thoroughly. In the presence of 0.1 M pyridine the total type II elimination and cyclization yield is 0.68; the maximum yield is 0.80.^{13,31} Given our conclusions above about the irreversibility of reaction 3, we can equate $k_{-X}\tau_{DR}$ with product ratios. Its value for 1-Cl is thus 0.10/0.80 or 0.125.

In a flash spectroscopic investigation to be reported separately,³² we have studied the 1,4-diradical formed from *p*-CF₃-1-Cl in benzene containing 0.1 M pyridine. The diradical decays with a lifetime of 27 ns and yields 14% of a longer lived ketyl radical. The diradicals formed from valerophenone and several ring-substituted valerophenones including *p*-CF₃, *p*-Cl, and *p*-Br have lifetimes of 35 ± 5 ns under the same conditions. This flash experiment confirms that a small fraction of the chloro diradical reacts as indicated in Scheme I and also sets k_{-Cl} equal to 4×10^6 s⁻¹.

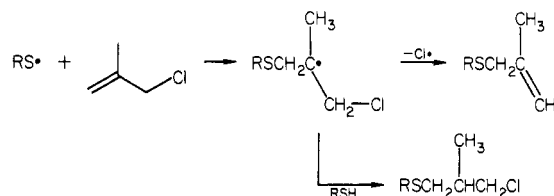
We are not certain whether the same τ_{DR} holds for 1-Br and 1-I. If such diradical lifetimes are determined primarily by rates of triplet \rightarrow singlet intersystem crossing (ISC),^{8,33} the major structural change that one could expect are heavy atom effects. Since para halogens and δ chlorine do not affect the lifetime significantly, any rate-determining ISC mechanism operating in these diradicals cannot be significantly augmented by weak heavy atom effects.⁸ Bromine and iodine atoms may, however, couple more strongly in the diradicals (see below).

The other extreme interpretation of diradical lifetimes is that they are determined primarily by rates of their chemical reactions. We reported several years ago that the 1,4-diradicals formed from ketones with electron-withdrawing δ substituents undergo relatively little disproportionation back to reactant ketone.³¹ Since disproportionation normally accounts for 60% of type II diradicals³¹ but only some 20% for 1-Cl, τ_{DR} for 1-Cl would then be double that found for unhalogenated diradicals, provided that the δ -substituent does not affect the rate of diradical cleavage. Such obviously is not the case.

Within the limitations of our understanding of the factors which determine diradical lifetimes, we can assign minimum values for

k_{-Br} of 3×10^8 s⁻¹ and for k_{-I} of $>5 \times 10^9$ s⁻¹. An activation energy of 7.5 kcal/mol has been estimated for cleavage of the 2-bromoethyl radical,³⁴ quite consistent with our measured k_{-Br} value, given an *A* factor of 10^{13} s⁻¹.

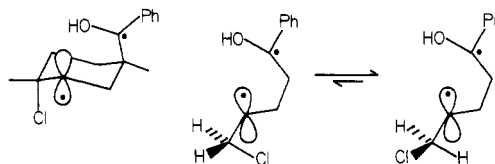
The value for k_{-Cl} is considerably larger than previously estimated, a value on the order of 10^{-4} s⁻¹ having been measured for chloroethyl radical in the gas phase.³⁵ This lower value is in accord with the expected thermodynamics of the reaction, a C-Cl bond being some 20 kcal/mol stronger than a C=C bond.³⁶ We investigated and eliminated the possibilities of ionic and cyclic transition states precisely because of this unexpectedly large value of k_{-Cl} . However, known chemistry already suggests that β -elimination of chlorine in solution is faster than suggested for gas-phase results. Hall reported that the addition of methyl mercaptan to allylic chlorides results in loss of chlorine.³⁷ Analysis



of reported product ratios as a function of mercaptan concentration indicates that the rate constants for loss of β chlorine and for reaction with mercaptan are comparable in magnitude. Our earlier biradical trapping results with mercaptan^{3,5} and these present results show that both reactions are also competitive for diradicals.

It appears that k_{-Cl} is much larger in solution than in the gas phase. One possible explanation for the difference is the well-known ability of benzene to complex chlorine atoms.³⁸ As discussed above, β -elimination from the diradical is probably irreversible. The analogous elimination from a monoradical may be partially reversible.

Efficiencies of Diradical β -Elimination. Comparison of 1-Cl and 3 reveals that the latter eliminates HCl in proportionately greater efficiency, almost no type II product being formed. In the diradical formed from 3, the axial chlorine is lined up in a perfect anti relationship with the singly occupied p orbital. The



maximum rate for elimination in the diradicals formed from **1** presumably occurs at a similar alignment; only a fraction of the diradicals exist in this conformation in equilibrium with other rotamers.

The process which leads to elimination of HX appears to have an intrinsic efficiency of only some 50%, that being the quantum yield for 1-Br, 1-I, and *trans*-4, the 1,4-diradicals from which presumably undergo only elimination. The 10% quantum yield of **2** from 1-Cl also accounts for only half the triplets which do not give type II products. Ionic readdition of HX presumably cannot occur in the presence of pyridine. Therefore, we conclude that the inefficiency occurs during elimination. Since the inefficiency involves the presence of a δ halogen but alkyl halides in general are not quenchers of triplet ketones, we conclude that the inefficiency occurs during γ -halogen abstraction rather than afterwards or independently. Such coupled chemistry and decay

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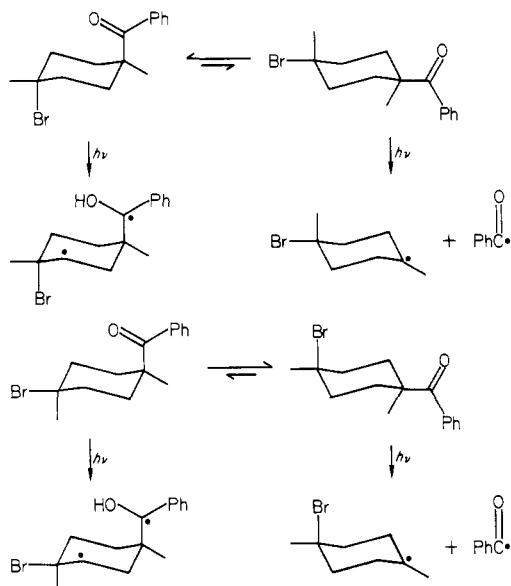
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is, in fact, characteristic of *singlet* type II reactions of aliphatic ketones^{1,39} but is unprecedented for triplet type II reactions. (The high intersystem crossing yields of 1 indicate only triplet reaction.) However, γ -hydrogen abstraction in these δ -halo ketones is unique in that the halogen seems to participate in the process. We shall return to the problem of inefficiency after considering this participation.

Participation by δ Halogen. As Table I indicates, the rate of triplet decay increases by a factor of 7.6 in going from 1-Cl to 1-I. We have already discussed why this increase in decay rate does not reflect some process competing with γ -hydrogen abstraction.⁴⁰ Our best interpretation of all the data is that $1/\tau_T = k_H$. The substantial inductive effects of δ substituents on k_H values have already been discussed in detail.¹³ The δ Cl lowers k_H to 18% its value in triplet valerophenone. The σ_I values for I and Br are slightly lower than for Cl⁴¹ so that the k_H values for 1-I and for 1-Br should be 45 and 10% greater, respectively, than for 1-Cl if only inductive effects are important. The actual $1/\tau$ values indicate that the δ -bromo and -iodo groups enhance the rate of γ -hydrogen abstraction by factors of 2.3 and 5.3 after correction for different σ_I values. These rate enhancements apparently represent another example of the "anchimeric assistance" which substantially accelerates hydrogen atom abstraction by bromine atoms.¹¹ As usual the n, π^* triplet benzoyl group mimics alkoxy radicals in displaying only minor⁴² "anchimeric assistance".

The behavior of 3 and 4 demonstrates the importance of orientation on the magnitude of the rate enhancements. All three ketones, like the unhalogenated model 7 studied by Lewis,¹⁹ form benzaldehyde and 2 from kinetically distinct triplets. The distinct triplets occur because ring flips of cyclohexanes are slower than triplet reactions.¹⁹ The benzaldehyde results from α -cleavage of the conformer with benzoyl equatorial in all four ketones. The observed rate constants are identical within experimental error for all four benzoylcyclohexanes plus two 4-benzoylpiperidines.²⁰ However, 3 and *trans*-4 undergo α -cleavage in very low quantum yields compared to *cis*-4 and 7. As explained above, the *trans* isomers exist primarily in the conformation with halogen and benzoyl both axial, such that very little of the light absorbed excites the isomer which undergoes α -cleavage. In contrast, 7 and *cis*-4



exist primarily in the conformation with benzoyl equatorial; these conformations absorb most of the light and then cleave in moderately high efficiency.

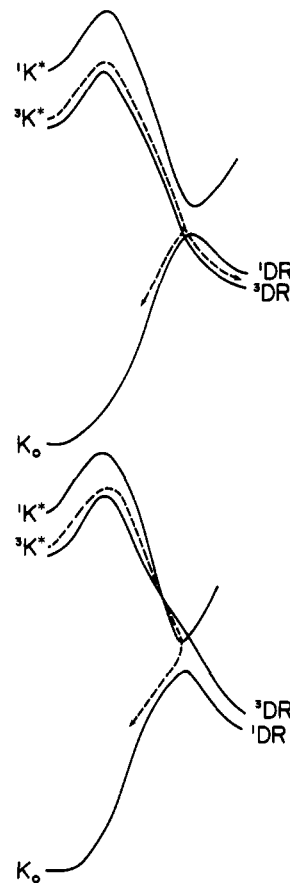


Figure 3. Potential energy diagram for triplet state γ -hydrogen abstraction with decay channel caused by intersystem crossing during reaction. Dashed line portrays energetic path leading to decay: (top) traditional scheme with triplet diradical lower in energy than singlet diradical; (bottom) zwitterionic stabilization of singlet diradical.

γ -Hydrogen abstraction in the appropriate conformers of *trans*-3 and -4 occurs with the δ halogen *trans*-periplanar to the γ -hydrogen being attacked. The Br/Cl k_H ratio is now 6, as opposed to the 2.5 ratio for 1-Br/1-Cl. In fact, *trans*-4 is more reactive than the unhalogenated model 7, whereas 3 is only 30% as reactive. The anchimeric assistance in 4 surpasses the opposing inductive effect.

In *cis*-4, only a few percent of the triplets are formed in an appropriate conformation for γ -halogen abstraction. We presume that ring flipping of the cyclohexyl radical part of the diradical is sufficiently rapid⁴³ for Br to be eliminated efficiently. The quantum yield for formation of 2 is lower than from *trans*-4, but not so much as expected from conformational equilibria. We suspect that some of the 2 came from prior *cis* \rightarrow *trans* isomerization of 4, as Lewis found for 1-benzoyl-4-*tert*-butylcyclohexane.¹⁹ The analytical method unfortunately required moderately high conversions. The triplet decay rate measured thus probably is not very accurate. However, it is only one-fourth as rapid as for *trans*-4, and we can cautiously conclude that the difference reflects the poor orientation in *cis*-4 for any assistance by bromine during hydrogen abstraction.

Although our results provide the first evidence for and the first quantitative measure of such radical "anchimeric assistance" in triplet ketone hydrogen abstraction, they do not provide any further understanding of this unusual phenomenon. However, its probable existence here does provide an explanation for the mysterious quenching which occurs during the reaction.

Anchimeric Quenching. Whether halogens assist in hydrogen abstraction by bridging or merely by specifically oriented hy-

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perconjugation,^{11,12} some free spin density must be transferred to the halogen during hydrogen abstraction. Therefore, the triplet-excited surface would be subject to an increasing heavy-atom effect as the reaction proceeds. We suggest that, by the time the excited surface crosses the ground-state surface, spin-orbit coupling in the incipient diradical is large enough to enhance the $T \leftrightarrow S$ interconversion rates. Therefore the excited surface can cross onto the ground surface before reaching the true triplet diradical state. This increase in quantum inefficiency from 1-Cl (0.10) to 1-Br (0.40) to 1-I (0.57) is what would be expected for a heavy-atom effect. The situation is very similar schematically to singlet-state γ -hydrogen abstraction, except that spin inversion during reaction is required. Figure 3 depicts the situation with one modification of the now familiar³⁹ potential energy surfaces for excited ketone hydrogen abstraction. The top sketch depicts the usual assumption of a lower energy triplet diradical. In the bottom sketch zwitterionic stabilization has caused the singlet diradical to be lower in energy. Shaik and Epitotis have discussed geometric factors which can induce spin-orbit coupling during triplet reactions,⁴⁴ including specifically homolysis of benzyl halides.⁴⁵ The mechanism we suggest here is very specific in that it involves the coincidence of participation by a heavy atom.⁴⁶ If we were working on the shores of Lake Mendota, we might be tempted to dub such a phenomenon "heavy anchimeric quenching", were it not that the phenomenon may not be very general.

Structure of 5-Halo 1,4-Diradical. Our results suggest bridging or its equivalent in the formation of δ -halo type II diradicals. One is not sure whether such transition state stabilization is necessarily maintained in the product diradical. Our results certainly do not further elucidate the nature of such "bridged" radicals. Inasmuch as free spin does reside on the δ halogen, spin-orbit coupling and $S \leftrightarrow T$ interconversion rates should be enhanced in the diradicals. Whether or not this "bridging" affects diradical lifetimes and the derived k_{-x} values depends on the factors discussed above. The effect is probably negligible for 1-Cl, but the values of k_{-Br} and k_{-I} must be viewed as minimum values.

Experimental Section

Preparation of Ketones. 1-Cl was prepared by the usual addition of phenylmagnesium bromide to Aldrich δ -chlorovaleronitrile^{13,47} and was purified by recrystallization from hexane, mp 50 °C: IR (KBr) 1685 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.90 (m, 4 H), 3.00 (t, 2 H), 3.58 (t, 2 H), 7.1–7.9 (m, 5 H); MS m/e 198, 196, 141, 120, 105.

1-Br was prepared analogously from Aldrich δ -bromovaleronitrile, mp 58.5 °C: IR (KBr) 1685 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.91 (m, 4 H), 2.99 (t, 2 H), 3.40 (t, 2 H), 7.1–7.9 (m, 5 H); MS m/e 242, 240, 161, 105.

1-I was prepared in 95% yield by treating 1-Br with a 10-fold excess of anhydrous KI in refluxing methyl ethyl ketone. It was purified after solvent removal by recrystallization from hexane, mp 71.5 °C: IR (KBr) 1685 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.92 (m, 4 H), 2.8–3.3 (overlapping t's, 4 H), 7.1–7.9 (m, 5 H); MS m/e 288, 161, 105.

p-Trifluoromethyl- δ -chlorovalerophenone was prepared by addition of δ -chlorovaleronitrile to *p*-trifluoromethylphenylmagnesium bromide, bp 105 °C (0.05 Torr): IR (neat) 1701 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.9 (m, 4 H), 3.0 (t, 2 H), 3.5 (t, 2 H), 7.5 (d, 2 H), 7.8 (d, 2 H); MS m/e 264.

p-Methoxy- δ -chlorovalerophenone was available from an earlier study.⁴⁸

1,4-Dimethyl-4-benzoylcyclohexene (5). Methyl methacrylate (40 g) was added dropwise to 250 mL of benzene containing 5 g of AlCl_3 . The solution was cooled in a water bath during addition of 28 g of isoprene. After being stirred overnight, the solution was poured onto cracked ice and HCl. The separated benzene layer was washed with dilute HCl, dried over sodium sulfate, and evaporated to give 52 g (80%) of crude 1,4-dimethyl-1-carbomethoxy-3-cyclohexene. This was hydrolyzed in 50:50 ethanol:water containing excess KOH. The cooled solution was

acidified with HCl. The acid was washed with water, then recrystallized from hexane to yield 42.5 g (90%) of 1,4-dimethyl-3-cyclohexene-carboxylic acid, mp 69 °C (lit: 69.5–70 °C).⁴⁹

The phenyl ketone **5** was prepared by refluxing for 3 h 2 equiv of phenyllithium (Aldrich) with the acid in ether. Aqueous workup produced **5** as an oil which polymerized upon attempted vacuum distillation: IR (neat) 1685, 1450, 945 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.33 (s, 3 H), 1.60 (s, 3 H), 1.9 (m, 6 H), 5.20 (br s, 1 H), 7.1–7.6 (m, 5 H).

trans-1,4-Dimethyl-4-chloro-1-benzoylcyclohexane (3). The ketone **5** was dissolved in glacial acetic acid, and dry HCl was bubbled in until the vinyl resonance at δ 5.2 no longer appeared in the NMR. The mixture was then poured into water and extracted with chloroform. The combined chloroform extracts were washed with saturated sodium bicarbonate, then dried, and evaporated. Addition of pentane to the crude oil followed by cooling and scratching with a glass rod resulted in crystallization. The recrystallized product had mp 65 °C: IR (CHCl_3) 1670, 1275 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.40 (s, 3 H), 1.50 (s, 3 H), 1.4–2.5 (m, 8 H), 7.1–7.6 (m, 5 H); ^{13}C NMR (CDCl_3) δ 27.5 ($\text{C}_1\text{-CH}_3$), 32.4 (C-2), 33.5 ($\text{C}_4\text{-CH}_3$), 38.6 (C-3), 47.6 (C-1), 71.5 (C-4), 127.0, 128.0, 131.4, 138.9 (Ph), 208.4 (C=O); MS m/e 250, 252 (M^+).

Crystallographic Data and X-ray Structure Analysis. Crystals of **3**, $\text{C}_{15}\text{H}_{19}\text{ClO}$, are monoclinic: space group $P2_1/c$; $a = 6.042$ (2), $b = 19.751$ (9), $c = 11.699$ (4) Å; $\beta = 99.15$ (2)°; $Z = 4$; $M_r = 250.77$; $\rho_{\text{calc}} = 1.208$ g cm^{-3} . Lattice dimensions were determined using a Picker FACS-I diffractometer and $\text{Mo K}\alpha_1$ (λ 0.70926 Å) radiation.

Intensity data were measured using $\text{Mo K}\alpha$ radiation ($2\theta_{\text{max}} = 45^\circ$), yielding 1816 total unique reflections including, based on $I > 2\sigma(I)$, 1258 observed data. The data were reduced,⁵⁰ the structures were solved by direct methods,⁵¹ and the refinement was by full-matrix least-squares techniques.⁵² The final R value was 3.6%. The final difference Fourier map showed densities ranging from +0.21 to -0.26 with no indications of misplaced or missing atoms. An ORTEP⁵³ drawing of the molecule is shown in Figure 1.

1,4-Dimethyl-4-bromo-1-benzoylcyclohexane (4). This was prepared from **5** exactly as was **3** except that HBr was added. After the initial crop of crystals was collected, concentration of the mother liquor and subsequent cooling resulted in another crop of crystals which were the low-melting *cis* isomer.

trans-4: mp 82 °C; IR (CHCl_3) 1660, 1210 cm^{-1} ; MS m/e 294, 296 (M^+); ^1H NMR (CDCl_3) δ 1.43 (s, 3 H), 1.73 (s, 3 H), 1.2–3.5 (m, 8 H), 7.1–7.6 (m, 5 H); ^{13}C NMR (CDCl_3) δ 27.5 ($\text{C}_1\text{-CH}_3$), 33.4 (C-2), 35.2 ($\text{C}_4\text{-CH}_3$), 40.1 (C-3), 47.6 (C-1), 70.8 (C-4), 127.5, 128.0, 130.9, 138.4 (Ph), 208.0 (C=O).

cis-4: mp 32 °C; IR (CHCl_3) 1675, 1205 cm^{-1} ; MS m/e 294, 296 (M^+); ^1H NMR (CDCl_3) δ 1.32 (s, 3 H), 1.84 (s, 3 H), 1.4–2.4 (m, 8 H), 7.1–7.6 (m, 5 H); ^{13}C NMR (CDCl_3) δ 21.8 ($\text{C}_1\text{-CH}_3$), 31.7 (C-2), 34.2 ($\text{C}_4\text{-CH}_3$), 38.6 (C-3), 46.4 (C-1), 69.0 (C-4), 127.5, 127.9, 130.6, 139.1 (Ph), 208.6 (C=O).

4-Benzoyl-1-butyl Tosylate. 1-I (4 g in 20 mL of CH_3CN) was added to 50 mL of CH_3CN containing 4.1 g of silver tosylate at 5 °C, with the entire set up protected from light. The solution was allowed to stir overnight while gradually warming to room temperature. Aqueous workup, extraction into ether and recrystallization from hexane-ether yielded off-white crystals, mp 59–61 °C: IR (CHCl_3) 3020, 1685, 1600, 1445, 1355, 1200, 1175 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.72 (m, 4 H) 2.37 (s, 3 H) 2.87 (t, 2 H) 3.64 (t, 2 H) 7.1–7.9 (m, 9 H).

ϵ -Iodohexanophenone. ϵ -Chlorohexanophenone¹³ was refluxed in NaI-saturated methyl ethyl ketone for 2 days. After filtration of the NaCl precipitate and solvent evaporation, the crude product was taken up in ether, washed, and dried. Recrystallization from hexane yielded white crystals: ^1H NMR (CDCl_3) δ 1.4–2.0 (m, 6 H) 2.90 (t, 2 H) 3.10 (t, 2 H) 7.1–7.4 (m, 3 H) 7.7–7.9 (m, 2 H).

Other Chemicals. Benzene was purified by treatment with sulfuric acid and distillation from P_2O_5 . Pyridine was distilled from barium oxide. Naphthalene was recrystallized from ethanol. Alkanes as internal standards were available from previous work. Chemical Sample Co. *cis*-1,3-pentadiene was used as received.

Identification of Photoproducts from 1. Acetophenone and its ring-substituted derivatives were identified by comparison of GC retention times with those of authentic samples under identical conditions. 4-

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Benzoyl-1-butene was collected by preparative GC (10% SE-30 column at 160 °C) from a sample of 1 g of 1-Br in 250 mL of benzene irradiated in an immersion well with a Pyrex-filtered 450-W mercury arc. Its spectroscopic properties were identical with those from an independently prepared sample (addition of phenylmagnesium bromide to 4-cyano-1-butene): IR (neat 1685, 1455, 1220, 1010, 920, 750, 696 cm^{-1}); ^1H NMR (CDCl_3) δ 2.50 (m, 2 H), 3.00 (t, 2 H), 4.8–5.3 (m, 2 H), 5.5–6.3 (m, 1 H), 7.2–8.0 (m, 5 H); MS m/e 160, 105, 77.

Identification of Photoproducts from 3 and 4. 1,4-Dimethyl-4-benzoyl-4-cyclohexene (**5**) was collected from an irradiated solution of **3** and shown to have identical spectroscopic characteristics to the synthetic precursor to **3**. Injection of unirradiated benzene solutions of **3** onto a 3% QF-1 column at 150 °C resulted in two peaks on the GC trace, in a 1:3 ratio. The lesser one corresponded to **5**. After 12 h irradiation of the solution, the second peak had totally disappeared and was therefore assigned to **3**. Only three product peaks appeared: one corresponding to **5**, one corresponding to benzaldehyde, and a small new one with a retention time slightly shorter than that of **3**. IR analysis of this solution showed a moderately intense absorption at 3500 cm^{-1} , suggesting the presence of the expected cyclobutanol. The benzene was removed and replaced with CCl_4 . Addition of Br_2 resulted in the precipitation of an orange solid which melted at 79 °C. Addition of Br_2 to authentic **5** resulted in a dibromide with a melting point at 83 °C. This dibromide did not yield **5** during GC analysis. Treatment with zinc dust of the dibromide prepared from irradiated **3** yielded **5**, as judged by GC analysis. A solution of **3** in benzene- d_6 containing 0.05 M pyridine was placed in a NMR tube, degassed, and sealed. Irradiation for 4 h at 313 nm produced a white precipitate; NMR analysis of the solution showed vinylic resonance at δ 5.2 identical with that of authentic **5**.

Irradiation of 4-Benzoylbutyl Tosylate. Benzene solutions 0.1 M in ketone were irradiated as usual. GC analysis of unirradiated solution showed only a large peak with the characteristic retention time of 4-benzoyl-1-butene. Analysis of irradiated solution also showed a large peak corresponding to acetophenone.

Irradiation of ϵ -Iodohexanophenone. A degassed benzene solution 0.17 M in ketone and 0.5 M in pyridine was irradiated at 313 nm. A white precipitate formed. GC analysis showed four photoproducts, the three most volatile having relative peak areas of 14:2:1. They were collected by GC analysis. The largest was acetophenone, as determined by its characteristic retention time and NMR spectrum. The second had identical GC retention time and ^1H NMR as an authentic sample of 5-benzoyl-1-pentene:¹³ δ 1.5–2.4 (m, 4 H), 2.92 (t, 2 H), 4.8–5.1 (m, 2 H), 5.3–6.0 (m, 1 H), 7.1–7.4 (m, 3 H), 7.7–7.9 (m, 2 H). The 14:2 area ratio of the two major products, when corrected for a 8:12 carbon ratio, corresponds to a 10:1 mole ratio. The other products were not identified.

Quantitative Studies. Generally, samples were irradiated in 13 \times 100 mm Pyrex tubes which had previously been degassed and sealed. Sample tubes were always irradiated in parallel with valerophenone¹⁴ or benzophenone-1,3-pentadiene¹⁷ actinometers on a rotating "merry-go-round".⁵⁴ The 313-nm region of a 450-W Hanovia mercury arc was isolated with an alkaline chromate filter solution⁴⁸ and the 365-nm region with a Corning No. 7-83 filter combination. Product and reactant concentrations were determined by GC analysis on $1/8$ in. columns with FID detectors. Responses were calibrated relative to alkane internal standards present in known concentration from 0.002 to 0.02 M. Varian 600 and 1200 gas chromatographs were used with Infatronics digital integrators. NMR spectra were recorded on Varian T-60 and CFT-20 spectrometers and mass spectra on a Perkin-Elmer-Hitachi RU-6.

Solutions of **1** were prepared containing *n*-hexadecane and *n*-heptadecane, which served as internal standards for GC monitoring of acetophenone and **2**, respectively. A 12 ft column containing 10.4% QF-1 and 2.2% Carbowax 20M in 60–80 mesh Chromosorb W was used at 120–130 °C. Acetophenone appearance from valerophenone actinometers and from attempts to quench butyrophenone with alkyl halides was monitored relative to 0.004 M tetradecane. Disappearance of 1-Cl and 1-Br was monitored relative to octadecane or eicosane as internal standard on a 6-column containing 5% SE-30 on Chromosorb G. Product yields from ring-substituted 1-Cl were determined on a 6 ft column containing 3% QF-1 on Chromosorb G at 145 °C, relative to 0.003 M hexadecane. Analyses of **3** and **4** used the same column, with tetradecane as standard for benzaldehyde appearance and pyridine disappearance, hexadecane for **5** appearance, and nonadecane for cyclic alcohol from **3**. Pentadiene isomerization was monitored at 50 °C on a 25 ft column containing 25% 1,2,3-tris(2-cyanoethoxy)propane on Chromosorb P.

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Supplementary Material Available: Final positional and thermal parameters (Tables IV and V), bond distances and angles (Table VI), and structure factors with standard deviations (Table VII) for **3** (10 pages). Ordering information is given on any current masthead page.

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Excited-State Prototropism in Esters of *o*-Hydroxy-2-Naphthoic Acids

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Abstract: The photophysical behavior of methyl 3-hydroxy-2-naphthoate (I) and phenyl 1-hydroxy-2-naphthoate (II) have been investigated. The former compound exhibits two emission bands. The longer wavelength band is characteristic of the excited-state zwitterion formed by rapid excited-state intramolecular proton transfer. The normally Stokes-shifted emissions of both I and II exhibit a nonexponential fluorescence decay. This is interpreted in terms of more than one excited state (originating from excitation of distinct ground-state conformers) emitting within the fluorescence band. The behavior of these compounds is compared to that of methyl salicylate.

Recently it has been suggested that the explanations of Sandros¹ and Klöpffer and Naundorf² for the photophysical behavior of methyl salicylate should be extended.³ Fluorescence quenching

measurements on the short wavelength emission band have indicated that there are two distinct contributions to this band. The interpretation was in terms of two "slowly" interconverting ground-state conformers, which upon excitation gave rise to emission in the short wavelength band. The suggested conformers are ones in which the phenolic proton is H bonded to the "ether" oxygen atom of the ester group (Figure 1a), and a nonintramolecularly H bonded, or "open-ring" conformer (Figure 1b). The

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