Solvent Effects on Type II Photoelimination of Phenyl Ketones[1]

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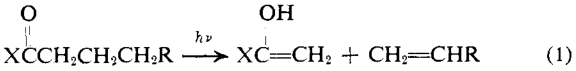
Abstract: Polar solvents appreciably enhance the quantum efficiency with which valerophenone undergoes photoelimination in solution. Quantum yields of acetophenone formation rise from 0.37–0.40 in hydrocarbon solvents to 0.90 in *t*-butyl alcohol. Quantum yields for total photoreaction rise from 0.45 in hydrocarbons to unity in alcohols and acetonitrile. Quenching studies indicate that the lifetime of the triplet excited state of the ketone does not vary more than a factor of four among various solvents. Consequently, it is inferred that the observed solvent effects arise from solvation of a hydroxy biradical intermediate rather than from any interaction with the excited state.

Norrish type II photoelimination, whereby carbonyl compounds containing γ-hydrogens split out olefins and the enols of smaller carbonyl compounds, has been intensively studied both in the gas phase[2] and in solution.[3] The reaction is noteworthy, among other reasons, for its low quantum efficiency.



$$\overset{\displaystyle O}{\overset{\|}{X C}}CH_2CH_2CH_2R \xrightarrow{h\nu} X\overset{\displaystyle OH}{\overset{|}{C}}{=}CH_2 + CH_2{=}CHR \qquad (1)$$

In work connected with determining the effects of solvent viscosity on triplet energy transfer, it was noted that irradiation of phenyl ketones in polar solvents produced acetophenone in greater quantum yields than those obtained in hydrocarbon solvents. This observation was surprising because it had been reported that there was no solvent effect on the photoelimination of butyrophenone[3b] and, if anything, the opposite solvent effect in the analogous reaction of esters.[4] Consequently, a thorough study was undertaken of solvent effects on the photochemistry of valerophenone. This ketone was chosen as a model phenyl ketone since its short triplet lifetime[3a] should mitigate the uncertainties connected with varying unknown concentrations of quenching impurities in different kinds of solvents.

Results

Solvent Effects on Quantum Yields. Degassed solutions containing 0.10 *M* valerophenone, 0.05 *M* hexadecane, and 0.01 *M* tetradecane were irradiated at 3130 A and 25° on a "merry-go-round" apparatus. Yields of acetophenone and per cent disappearance of valerophenone were then determined by glpc analysis. Conversions ranged from 5 to 25% in different determinations. These yields were converted to quantum yields by parallel irradiation and ultraviolet analysis of benzophenone–benzhydrol actinometer solutions.[5] The quantum yield for disappearance of 0.05 *M* benzophenone in degassed benzene containing 0.20 *M* benzhydrol was taken as 0.85.[5,6] The quantum yields obtained in different solvents are recorded in Table I.

Table I. Solvent Effects on Quantum Yields of Valerophenone Photoreactions

Solvent	$\Phi_{+\mathrm{PhCOMe}}$	$\Phi_{-\mathrm{PhCOBu}}$
Benzene	0.37	0.44
Hexane	0.40[a]	0.46
t-Butyl alcohol	0.90[b]	1.0
Isopropyl alcohol	0.68	1.0
Ethanol	0.70[c]	1.0
Acetonitrile	0.85	1.0

[a] This value is the same in a dozen different alkanes. [b] This value is the same in three different tertiary alcohols. [c] This value is the same in five different primary alcohols: I. Kochevar, unpublished results.

The quantum yield of acetophenone formation rises from 0.37–0.40 in hydrocarbon solvents to 0.90 in *t*-butyl alcohol, while the total quantum yield for disappearance of valerophenone rises from 0.45 in hydrocarbons to 1.00 in all alcohols and in acetonitrile. Two barely separated peaks with the correct retention times for the two 1-phenyl-2-methylcyclobutanols appeared on the glpc traces and accounted for 15% of the reacted ketone in hexane and acetonitrile, 10% in the alcohols. The two peaks had a 2:1 area ratio in all the polar solvents, very similar to the *trans/cis* ratio obtained by LaCount and Griffith in acetone,[7] but around a 5:1 ratio in hexane. Thus acetophenone and cyclobutanol formation account for all the photoreactivity of valerophenone in "unreactive" solvents. The slightly lower quantum yields of acetophenone formation in ethanol and 2-propanol relative to *t*-butyl alcohol and acetonitrile are undoubtedly due to a small amount (~20%) of competing photoreduction, although no search was made for pinacols.

Effect of Small Concentrations of Alcohol. Degassed hexane solutions containing 0.20 *M* valerophenone, 0.005 *M* tetradecane, and various concentrations of *t*-butyl alcohol were irradiated simultaneously at 3130 A. Quantum yields of acetophenone formation were then determined by glpc analysis. The results are listed in Table II and depicted in Figure 1. Even very low concentrations of the alcohol are strikingly effective

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[1] This work was supported by a grant from the National Science Foundation. For a preliminary account, see P. J. Wagner, *Tetrahedron Letters*, 1753 (1967).

[2] (a) See J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, p 382, for a review; (b) C. H. Nicol and J. G. Calvert, *J. Am. Chem. Soc.*, **89**, 1790 (1967).

[3] (a) P. J. Wagner and G. S. Hammond, *ibid.*, **88**, 1245 (1966); (b) E. J. Baum, J. K. S. Wan, and J. N. Pitts, Jr., *ibid.*, **88**, 2652 (1966); (c) D. R. Coulson and N. C. Yang, *ibid.*, **88**, 4511 (1966).

[4] P. Ausloos, *ibid.*, **80**, 1310 (1958).

[5] W. M. Moore and M. Ketchum, *ibid.*, **84**, 1368 (1962).

[6] In making quantum yield determinations on a "merry-go-round" apparatus, we have found it best to employ actinometers which are irradiated just as long as the samples. Use of a standard ferrioxalate actinometer is precluded by the deleterious effects of Lansing water flowing through East Lansing pipes. So much iron is deposited in the cooling jacket of the immersion well that escaping light intensity tends to fluctuate markedly with time.

[7] R. B. LaCount and C. E. Griffith, *Tetrahedron Letters*, 1549 (1965).

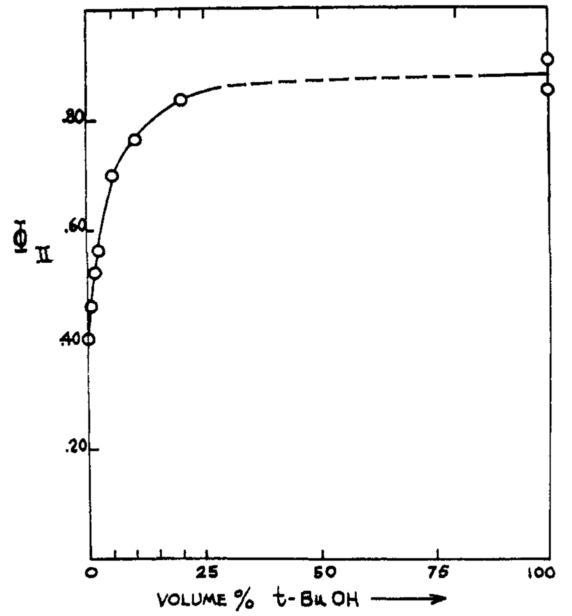

Figure 1. Variation in the quantum yield of acetophenone formation as a function of the composition of a mixed *t*-butyl alcohol-hexane solvent system.

at enhancing the quantum yield, the ultimate effect being reached at ~20% alcohol.

Table II. Quantum Yield of Acetophenone Formation upon Irradiation of Valerophenone in Mixed Hexane-*t*-Butyl Alcohol Solvents

t-BuOH, %	Φ_{PhCOMe}	*t*-BuOH, %	Φ_{PhCOMe}
0	0.40	10	0.77
0.5	0.46	20	0.85
1	0.52	100	0.90
2	0.57		

Table III. Quenching Constants for Triplet Valerophenone

Solvent	$k_q\tau$, M^{-1}	$k_q \times 10^{-9}$, M^{-1} sec^{-1}	$\tau \times 10^9$, sec	$1/\tau \times 10^{-8}$, sec^{-1}
Benzene	36	5.0	7.2	1.4
Hexane	78	11.0	7.2	1.4
Cyclooctane	30	4.2	7.2	1.4
t-Butyl alcohol	40	2.3	14.4	0.7
Acetonitrile	38	11.0	3.6	2.8
Acetone	47	11.0	4.2	2.4

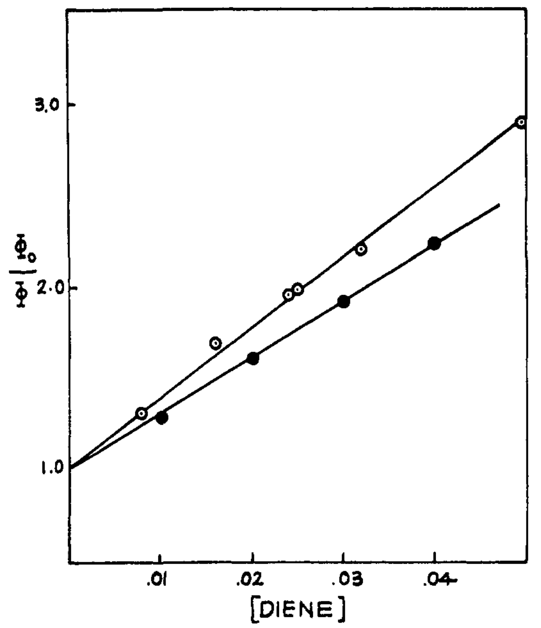

Figure 2. Stern-Volmer plot for quenching of acetophenone formation by 2,5-dimethyl-2,4-hexadiene from irradiation of valerophenone: ⊙, *t*-butyl alcohol solvent; ●, cyclooctane solvent.

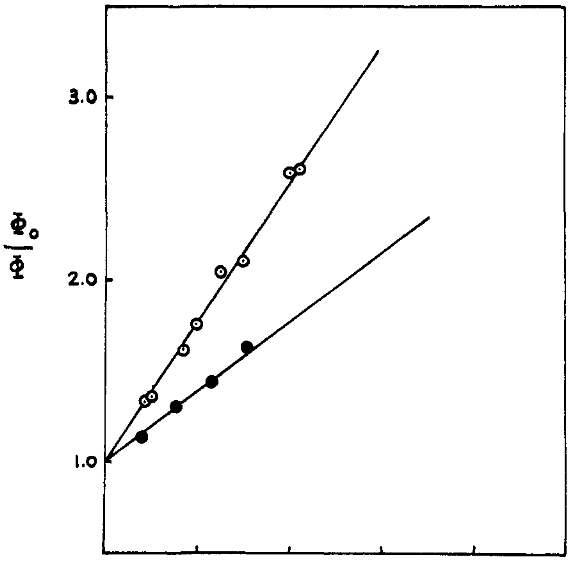

Figure 3. Stern-Volmer plot for quenching of acetophenone formation by 2,5-dimethyl-2,4-hexadiene from irradiation of valerophenone: ⊙, hexane solvent; ●, acetonitrile solvent.

Quenching Studies. Degassed solutions containing 0.10 or 0.20 *M* valerophenone, 0.005 *M* tetradecane, and various concentrations of 2,5-dimethyl-2,4-hexadiene as quencher (0.002-0.10 *M*) in several different solvents were irradiated in parallel at 3130 or 3660 A. Relative quantum yields of acetophenone formation were then determined as usual by glpc analysis. Figures 2 and 3 show some Stern-Volmer plots obtained in a few solvents. Table III lists the slopes of the linear Stern-Volmer plots in all the solvents, the values of which equal $k_q\tau$, where k_q is the rate constant for quenching of the triplet ketone by the diene in a given solvent and τ equals the lifetime of triplet valerophenone in that solvent. Also included in Table III are best estimates of k_q and τ. These were calculated as follows. It is now well established that the average maximum rate constant for triplet energy transfer in benzene at 25° equals 5×10^9 M^{-1} sec^{-1}.[8] A value of τ in benzene of 7.2×10^{-9} sec is thus indicated, and this value is assumed to remain constant in all hydrocarbon solvents. The small fluctuation in τ in widely different solvents (see below) attests to the probable accuracy of this assumption. Studies to be published[9] indicate that in solvents as viscous as tertiary alcohols, values

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[8] (a) H. J. L. Backstrom and K. Sandros, *Acta Chem. Scand.*, **16**, 958 (1962); (b) K. Sandros, *ibid.*, **18**, 2355 (1964); (c) W. G. Herkstroeter and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 4769 (1966).

[9] P. J. Wagner, Abstracts, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April, 1967, R118.

of k_q are inversely proportional to viscosity and therefore equal to the rate of diffusion. In particular, the value of $k_q\tau$ in an alkane with the same viscosity as *t*-butyl alcohol is ~20 M^{-1}, half the value observed in the alcohol. If k_q can be considered to have the same diffusion-controlled value in such different solvents,[10] τ would appear to be twice as large in *t*-butyl alcohol as in "inert" hydrocarbon solvents. Figure 2 demonstrates the same fact in another way. *t*-Butyl alcohol is almost twice as viscous as cyclooctane, yet quenching is slightly more efficient in it than in the alkane.

Acetone, acetonitrile, and hexane all have the same viscosity, and a value of 1.1×10^{10} M^{-1} sec^{-1} for k_q is indicated from the assumed 7.2×10^{-9} sec value of τ in hexane. This value of k_q is probably the same for all three solvents since (1) it is less than the diffusion-controlled rate, and (2) Ware and Novros have shown that the diffusion rate is the same in acetonitrile and hexane.[11] Therefore, in these two polar aprotic solvents, τ appears to be about one-half as large as it is in "inert" hydrocarbons.

Discussion

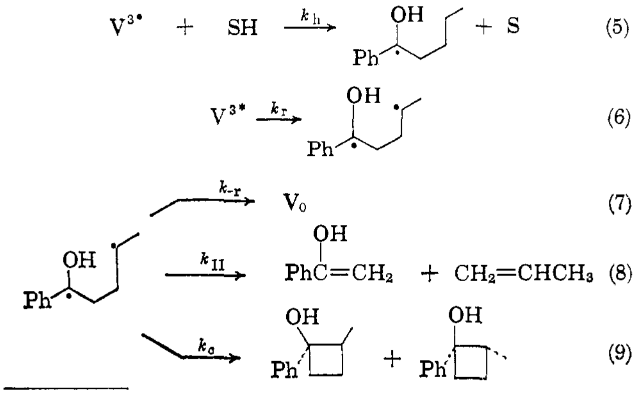
That a ketone with a triplet lifetime of only 7.2×10^{-9} sec should react with only 46% quantum efficiency is rather remarkable, since there are no known physical mechanisms for such rapid radiationless decay of excited states. We have previously suggested that the normal inefficiency arises from reversible transfer of a γ-hydrogen between the γ-carbon and the carbonyl oxygen.[3a] Coulson and Yang[3c] have reported results which demand that a γ-hydrogen be directly involved in whatever process returns >50% of the excited ketone molecules intact to their ground state. It is conceivable that there exists some particularly effective vibronic coupling of γ-C–H bonds with the excited carbonyl so that the excited state is deactivated rapidly and directly in competition with chemical reaction(s) to yield products. The solvent effects now reported do not seem to support this latter possibility.

Following is a complete mechanistic scheme for the photoreaction of valerophenone

$$V_0 \xrightarrow{h\nu} V^{1*} \xrightarrow{\sim 100\%} V^{3*} \qquad (2)$$

$$V^{3*} \xrightarrow{k_d} V_0 \qquad (3)$$

$$V^{3*} + Q \xrightarrow{k_q} V_0 + Q^* \qquad (4)$$



where V_0, V^{1*}, and V^{3*} represent ground state, lowest excited singlet, and lowest triplet valoerphenone; Q is a quencher molecule; and SH is a reactive solvent molecule. Since all the reactions of phenyl ketones occurs from a triplet state,[3] it is assumed that a biradical intermediate is involved.

The problem to be decided is whether 54% of the excited triplets return to the ground state *via* reaction 3, reaction 7, or some combination of the two. If internal conversion (3) accounts for all the inefficiency in inert solvents, $\tau = 1/(k_d + k_r)$. However, if reversible γ-hydrogen transfer (7) accounts for all the inefficiency, $\tau = 1/k_r$. Therefore, until this question is answered, the value for k_r can be estimated only to lie in the range of $0.6–1.4 \times 10^8$ sec^{-1} in hydrocarbon solvents. However, if the estimates of τ in Table III are correct, k_r equals 0.7×10^8 sec^{-1} in alcohols and about 2.8×10^8 sec^{-1} in acetonitrile, since the total quantum yield of unity in these solvents indicates that $k_d << k_r$.

In terms of the mechanistic scheme, the relatively small solvent effects on τ and the enhanced quantum efficiencies produced by polar solvents can mean either of two things: (1) polar solvents drastically decrease k_d while having little effect on k_r, or (2) polar solvents drastically decrease k_{-r} with respect to k_{II} and k_c.

As mentioned above, if k_d does have the unusually large value of 0.8×10^8 sec^{-1}, some sort of direct interaction between γ-hydrogens and the excited carbonyl must be responsible. It does not seem probable that any kind of solvation could prevent this physical interaction without also severely decreasing the rate of the chemical reaction between the same two moieties. Moreover, it would appear hazardous to postulate any strong polar solvation of the ketone triplet. Krishna and Goodman[12] have provided spectroscopic evidence that diazines are not hydrogen bonded in their n,π* triplet states. Similar behavior would be expected of ketone triplets, since it is well known that they possess the n,π* configuration when reactive. The blue shifts caused by polar solvents on the ultraviolet spectra of ketones are another manifestation of the lowered polarity of n,π* excited states relative to their ground states. The actual n → π* transition almost completely removes an electron from the carbonyl oxygen, making the oxygen electron deficient (and chemically reactive[13]) and sharply decreasing the dipole moment of the carbonyl group. Consequently, only weak dipole–dipole interactions with solvent would be expected.

It is entirely reasonable, if not readily predictable, that polar solvents could retard reaction 7. The hydroxyl proton of the postulated biradical intermediate ought to be able to form strong hydrogen bonds to polar solvents and thus impede its transfer back to the γ-carbon. Such hydrogen bonding would not be expected to affect reactions 8 and 9, so the net effect is that most or all of the solvated biradical yields products.

The slight changes noted in the yields and ratios of *cis*- and *trans*-1-phenyl-2-methylcyclobutanol are in accord with this hypothesis. In the inert solvent hexane, a 5:1 *trans*:*cis* ratio and a total yield (of reacted ketone) of 15% are observed. In alcohols, the total yield of cyclobutanols drops to 10% and the *trans*:*cis* ratio falls to 2:1. Both effects are consistent with a

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[10] There is experimental support for this assumption: A. D. Osborne and G. Porter, *Proc. Roy. Soc.* (London), **A284**, 9 (1965).

[11] W. R. Ware and J. S. Novros, *J. Phys. Chem.*, **70**, 3247 (1966).

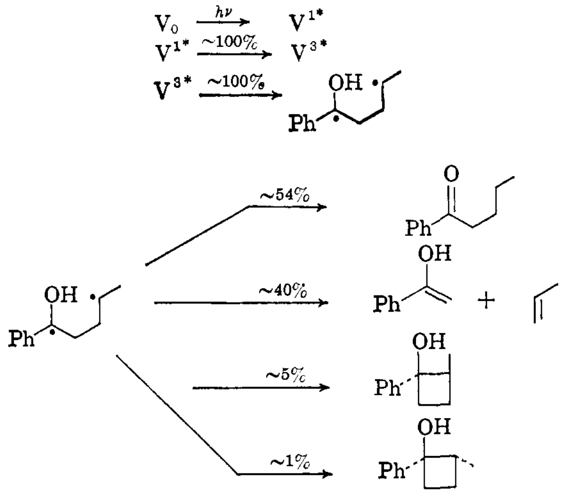
[12] V. G. Krishna and L. Goodman, *J. Am. Chem. Soc.*, **83**, 2042 (1961).

[13] C. Walling and M. J. Gibian, *ibid.*, **87**, 3361 (1965).

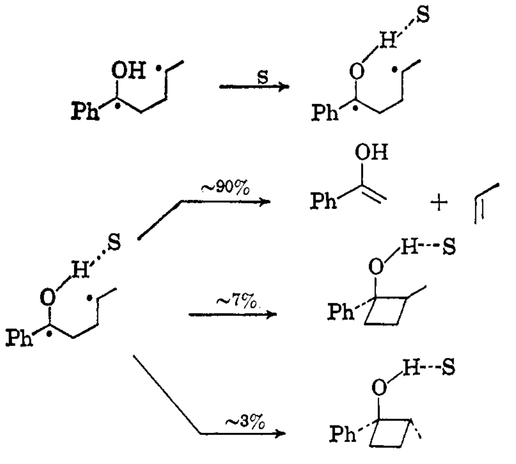
small amount of steric interference between hydrogen-bonded solvent molecules and the 2-methyl group in formation of the *trans* isomer.

The preferred explanation of these solvent effects yields the conclusion that the excited triplet states of phenyl ketones undergoing type II photoelimination *all* react to form a biradical intermediate and values of k_r equal $1/\tau$. Any net quantum inefficiency must be ascribed to secondary reactions of this primary photoproduct. Such behavior may well be quite general, there being several examples of ketones which have quite short triplet lifetimes, yet undergo photochemical changes in relatively low quantum efficiency.

From the above conclusions the following scheme can be drawn to describe the fate of all the photons absorbed by valerophenone in the absence of quenchers or reactive solvents.



In the presence of polar solvent



Some quantitative discussion of the data in Table II and Figure 1 is possible. At low concentrations of alcohol in hexane, the increase in quantum yield is fairly linear with alcohol concentration. In pure hexane, only 45% of the triplets react, while in hexane containing 1% *t*-butyl alcohol, ~60% react. Therefore a concentration of 0.1 *M* alcohol molecules causes ~30% of the excited states which otherwise would have returned to ground-state ketone to instead yield products. The rate of diffusion calculated in hexane is 2.7×10^{10} M^{-1} sec^{-1},[10] so the fastest any intermediate could collide with alcohol molecules is 2.7×10^{9} sec^{-1}. If every encounter with the intermediate responsible for inefficiency were effective at removing the inefficiency, a maximum rate of decay of 9×10^{9} sec^{-1} is indicated for that intermediate. The true rate of decay may be somewhat slower, since every encounter between intermediate and alcohol molecules may not be effective at preventing decay back to the ground-state ketone. However, with the actual lifetime of the triplet state known from quenching studies, encounters between triplet ketone and alcohol molecules could be no more than 1–2% effective at preventing decay if the triplet itself were responsible for the normal quantum inefficiency. Since this possibility has been fairly well ruled out by other evidence, and since hydrogen bonds are probably formed with good efficiency, one can place a lifetime of somewhat longer than 10^{-10} sec on the biradical intermediate postulated to intervene in the photoelimination of valerophenone.

Experimental Section

Chemicals. Aldrich valerophenone was distilled under reduced pressure and then recrystallized twice from pentane. Aldrich 2,5-dimethyl-2,4-hexadiene was recrystallized twice from itself. All hydrocarbon solvents were reagent grade materials treated with sulfuric acid, dried, and distilled from phosphorus pentoxide. Alcohols were reagent grade and distilled, usually from sodium. Spectroquality acetonitrile was distilled from calcium hydride and acetone was reagent grade distilled from permanganate and dried over Drierite.

Quantum Yield Determination. Solutions were prepared in various solvents as described in the Results section, and 2.8 ml of each was placed in separate Pyrex 13 × 100 tubes. Each sample was degassed three times to 0.005 torr and sealed *in vacuo*. In a given run all tubes were irradiated in parallel for the same length of time on a "merry-go-round" apparatus which assured that each sample absorbed the same intensity of light. The 3130-A line of a 450-w Hanovia medium-pressure mercury arc was isolated with a 1-cm path of 0.002 *M* potassium chromate in a 1% aqueous solution of potassium carbonate. Analyses were performed on both Aerograph Hy-Fi 600-D or Hy-Fi III 1200 gas chromatographs with flame ionization detectors and a 6 ft × $^1/_8$ in. column containing 4% QF-1 and 1% Carbowax 20M on 60–80 AW, DMSC-treated Chromosorb G set at 100 or 140°. The mole ratio:area ratio response of the machines was calibrated for acetophenone and tetradecane or hexadecane mixtures, so that yields of acetophenone could be measured accurately. Per cent reaction of valerophenone was determined by direct comparison of ketone–hexadecane area ratios before and after irradiation. It was assumed that the cyclobutanol isomers produced the same glpc response as each other and as valerophenone.

Quenching studies were as previously described.[14]

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(14) P. J. Wagner, *J. Am. Chem. Soc.*, **89**, 2820 (1967).