

Type II Photoprocesses of Phenyl Ketones. Evidence for a Biradical Intermediate

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Abstract: Phenyl alkyl ketones generally undergo type II photoelimination and photocyclization solely from their lowest n, π^* triplet states. Photolysis of β, γ -diphenylbutyrophenone yields no triplet stilbene, which would be formed in a concerted elimination. It is concluded that γ -hydrogen abstraction to yield a 1,4 biradical is faster than the energetically allowed concerted elimination. It is suggested that the sequence triplet \rightarrow biradical \rightarrow products presents the facile path for T \rightarrow S spin inversion which a concerted elimination cannot. Quantum yields for elimination, cyclization, and racemization of (4S)-(+)-4-methyl-1-phenyl-1-hexanone (I) total very close to unity. Added alcohol increases product quantum yields while decreasing racemization. The study of γ -deuterated phenyl *n*-octyl ketone reveals a k_H/k_D value of 4.8 for triplet state reaction. All this behavior would be expected from a biradical intermediate formed with 100% efficiency from the triplet and confirms earlier suggestions that low type II quantum yields in hydrocarbon solvents are caused by disproportionation of the biradical back to reactant ketone. In this regard, the total lack of any correlation between type II quantum yields and triplet-state lifetimes for different ketones makes sense only if quantum yields are determined solely by the partitioning of the biradical intermediates. Quenching and deuterium labeling studies reveal that alkyl thiols efficiently trap the biradicals from valerophenone and γ -methoxyvalerophenone, suggesting a solvated biradical lifetime $\sim 10^{-6}$ sec. Any trapping of the biradical from valerophenone by tributylstannane is hidden by the very rapid reduction of triplet ketone. A maximum value for the unsolvated biradical lifetime in heptane is estimated to be 2×10^{-7} sec. Some residual optical activity in the cyclobutanols obtained from (+)-I suggests that the biradical does not live quite long enough to establish complete rotational equilibrium about the β, γ C-C bond.

It was 5 years ago that the excited states involved in the much studied Norrish type II photoelimination of ketones were finally identified. With phenyl ketones, only triplets² (presumably n, π^* ³) react, while both n, π^* singlets and triplets of aliphatic ketones react.⁴ At that time there had been no systematic quantitative study of structure-reactivity relationships for any photoreaction. Encouraged by the ease of obtaining excited state rate constants from Stern-Volmer quenching studies² and feeling that prior knowledge of triplet state behavior was necessary for efficient analysis of aliphatic ketone photoreactions, we embarked on a thorough investigation of the type II reactions of phenyl ketones, various aspects of which are reported in this series of papers. In this first paper we consider the mechanism of the reaction.

In 1958, the Yangs observed that cyclobutanol formation accompanies elimination⁵ (henceforth we shall refer to them together as the type II processes) and suggested that both processes proceed through a common 1,4 biradical intermediate. This suggestion was compelling not only for its mechanistic economy but also because the known ease of intermolecular hydrogen atom abstraction by excited ketones demands an intramolecular counterpart. We later opined² that the low quantum yields characteristic of type II reactions in hydrocarbon solvents are due to disproportionation of the same biradical intermediate back to ground state reactant ketone. This suggestion received powerful

support from the observation that quantum yields for type II processes of triplet ketones rise to unity in polar solvents, presumably because hydrogen bonding by the hydroxy biradical to solvent inhibits its disproportionation reaction but not its cyclization or cleavage.^{6,7}

Unfortunately, despite the consistency of such results with the idea of a biradical intermediate, none of them can be considered unequivocal proof that the type II reactions proceed *solely* through such an intermediate. Therefore, we have studied a model compound whose triplet state elimination could energetically proceed concertedly. Likewise, we have studied an optically active ketone with an asymmetric γ carbon in order to ascertain how much racemization takes place during reaction. Such racemization would, of course, be a necessary consequence of a biradical intermediate, provided it is long-lived enough. Finally, we have estimated the biradical lifetime by trapping studies.

Results and Discussion

Intermediacy of Triplet States. Ample proof has been published that the type II reactions of most phenyl alkyl ketones proceed solely from triplet states. For example, after >99% of the photoelimination of γ -phenylbutyrophenone is quenched by added diene, the Stern-Volmer plot is still linear.⁸ The maximum possible singlet quantum yield is thus only 0.001. Likewise, use of the ketones to photosensitize the cis-trans isomerization of 1,3-pentadiene⁹ establishes an inter-system crossing yield of 1 ± 0.01 .

Nature of the Reactive Triplet. Analysis of the phosphorescence of phenyl alkyl ketones is not totally

(1) (a) Alfred P. Sloan Fellow, 1968-1972. (b) Work on ketones I, II, and nonanophenone from Ph.D. Thesis, Michigan State University, 1971.

(2) P. J. Wagner and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 1245 (1966).

(3) E. J. Baum, J. K. S. Wan, and J. N. Pitts, Jr., *ibid.*, **88**, 2652 (1966).

(4) (a) P. J. Wagner and G. S. Hammond, *ibid.*, **87**, 4009 (1965); (b) T. J. Dougherty, *ibid.*, **87**, 4011 (1965).

(5) N. C. Yang and D. H. Yang, *ibid.*, **80**, 2913 (1958).

(6) P. J. Wagner, *ibid.*, **89**, 5898 (1967).

(7) R. D. Rauh and P. A. Leermakers, *ibid.*, **90**, 2246 (1968).

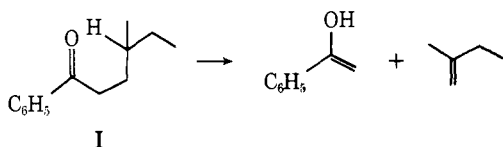
(8) P. J. Wagner and I. Kochevar, *ibid.*, **90**, 2232 (1968).

(9) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

straightforward, but characteristically short phosphorescence lifetimes at 77°K indicate lowest n, π^* triplets.¹⁰ It is always assumed that the n, π^* triplet is reactive in hydrogen abstraction reactions when it is the lowest energy triplet.

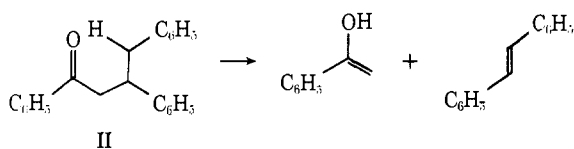
Possible Concertedness. We sought first to establish whether triplet state type II elimination can proceed concertedly. Such a process should be most rapid if spin is conserved, *i.e.*, if one product is formed as a triplet. There is nothing resembling agreement on the part of chemists regarding the effects of spin on rates of triplet state reactions, but the retarding effects of spin changes on electronic conversions within the same molecule surely ought to extend to chemical reactions of excited states.¹¹ Given this assumption, one concludes that, in the absence of effects enhancing spin-orbit coupling, a concerted triplet state reaction ${}^3R^* \rightarrow {}^3P^*$ will proceed rapidly only if the exothermicity of ${}^3R^* \rightarrow {}^1P_0$ is greater than the triplet excitation energy (${}^3P^* \leftrightarrow {}^1P_0$) of the product.

Consideration of bond energies and heats of formation (Appendix I) suggests a $\Delta H = +30$ kcal and a $\Delta S = +30$ eu for the reverse ene reaction of 4-methyl-1-phenyl-1-hexanone (γ -methylcaprophenone) (I).



The 0-0 phosphorescence band of phenyl alkyl ketones at room temperature in benzene occurs at 397 nm (72.0 kcal).¹² Therefore, the type II reaction from triplet I is 42 kcal exothermic, not enough to produce either olefin product in its triplet state (E_T for styrene is approximately 62 kcal,^{9,13} E_T for alkenes ~ 80 kcal¹⁴).

On the other hand, similar thermochemical estimates indicate that the type II elimination of triplet β, γ -diphenylbutyrophenone (II) is 50 kcal exothermic, just enough to produce *trans* and especially twisted triplet stilbene.^{15,16}



We synthesized II by adding benzyl Grignard to chalcone.¹⁷ Degassed benzene solutions 0.35 *M* in ketone were irradiated at 366 nm, where the stilbene product does not absorb. Acetophenone and stilbene are formed in equal yields. Caldwell and Fink have reported $\sim 20\%$ of an additional product presumed to

(10) P. J. Wagner, M. J. May, A. Haug, and D. R. Graber, *J. Amer. Chem. Soc.*, **92**, 5269 (1970).

(11) This statement is a corollary of Hammond's suggestion that chemical reactions of excited states be treated as radiationless decay processes: G. S. Hammond, *Advan. Photochem.*, **7**, 373 (1969).

(12) (a) R. G. Zepp, unpublished results; (b) P. J. Wagner, M. J. May, and A. Haug, *Chem. Phys. Lett.*, **13**, 545 (1972).

(13) D. F. Evans, *J. Chem. Soc.*, 1351 (1957).

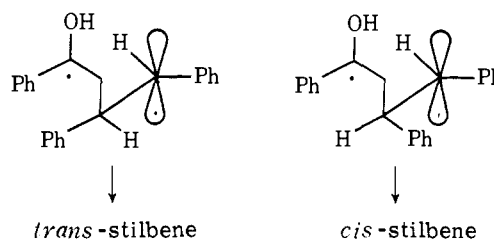
(14) A. J. Merer and R. S. Mullikan, *Chem. Rev.*, **69**, 639 (1969).

(15) J. Saltiel, *J. Amer. Chem. Soc.*, **89**, 1036 (1967); **90**, 6394 (1968).

(16) Including the entropy gain, the total free-energy charge for cleavage of triplet II is -59 kcal. It is interesting to speculate whether any of the $T\Delta S$ energy released—or only the enthalpy—is available for conversion into electronic energy of a product.

(17) P. J. Hamrick and C. R. Hauser, *J. Amer. Chem. Soc.*, **81**, 494 (1959).

be the expected 1,2,3-triphenylcyclobutanol.¹⁸ The quantum yield of type II elimination is subject to the usual solvent effect,⁶ rising from 0.11 in benzene to 0.19 in the presence of 2 *M* *tert*-butyl alcohol. Most importantly, at low conversions the stilbene product is 98.6% *trans*.^{18,19} Since triplet stilbene is known to decay to a 60:40 *cis*-*trans* mixture,^{14,15} our results set the maximum amount of concerted reaction at 1%. The normal solvent effect and competing cyclization are thus characteristic of the $>99\%$ nonconcerted reaction pathway. Although only 0.01% *cis*-stilbene would be expected at thermal equilibrium, the actual product distribution is kinetically controlled and most likely reflects a 99:1 conformational preference in the likely biradical intermediate.



Two sidelights demand comment. First, at conversions greater than 10%, the percentage of *cis*-stilbene from II increases because of sensitized isomerization of the initially formed *trans*-stilbene. We have reported elsewhere that the very short triplet lifetime of II minimizes the importance of this experimental problem.²⁰ Second, it is conceivable that the exothermicity of cleavage of triplet II is sufficient to populate an undetectable twisted triplet state of the enol product. We cannot present experimental evidence against such a possibility. Unfortunately, few photo-reactions are known which produce electronically excited products. It would be amazing, however, if virtually all the electronic energy were dumped into the product with the higher excitation energy, especially when the two products have quite similar chromophores. If electron-impact induced reactions can be used as an analogy, we can point out that in the McLafferty rearrangement—the mass spectral analog of type II elimination—the olefin fragment with the lower ionization potential preferentially retains the charge.²¹

In summary, consideration of thermochemistry indicates that triplet I cannot react concertedly to yield a triplet product while triplet II could but does not. Since the most likely nonconcerted reaction is γ -hydrogen abstraction to yield a biradical, the behavior of a ketone with an asymmetric γ carbon is of obvious interest.

(4*S*)-(+)-4-Methyl-1-phenyl-1-hexanone (+)-I, [α]_D²⁵ +9.81° (benzene), was synthesized by Friedel-Crafts acylation of benzene with (*S*)-(+)- γ -methylcaproyl chloride, which in turn was prepared *via* alkylation of malonic ester with the tosylate from (*S*)-(-)-2-methyl-1-butanol, [α]_D²⁵ -5.80° (neat). The only detectable reaction products from irradiation of the ketone in

(18) R. A. Caldwell and P. Fink, *Tetrahedron Lett.*, 2987 (1969).

(19) For a preliminary communication, see P. J. Wagner and P. A. Kelso, *ibid.*, 4152 (1969).

(20) P. J. Wagner, P. A. Kelso, A. E. Kemppainen, A. Haug, and D. R. Graber, *Mol. Photochem.*, **2**, 81 (1970).

(21) F. W. McLafferty, "Interpretation of Mass Spectra," W. A. Benjamin, New York, N. Y., 1966.

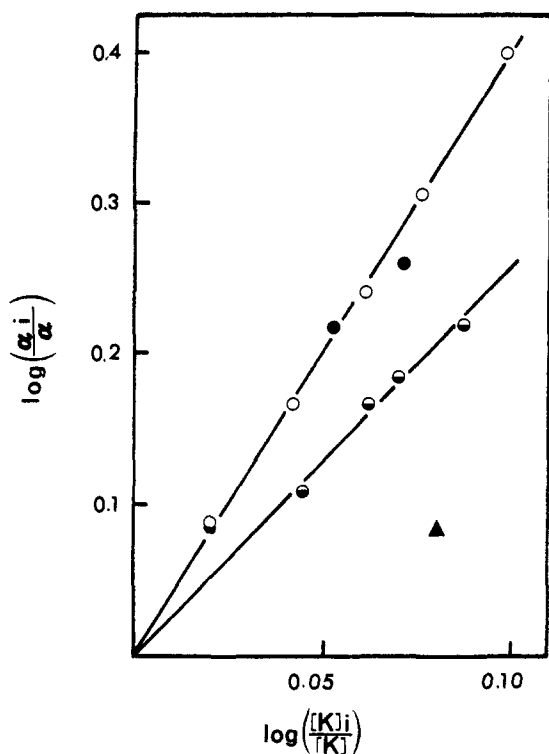


Figure 1. Optical activity of 0.1 *M* solutions of (4*S*)-(+)-4-methyl-1-phenyl-1-hexanone as a function of conversion: O, benzene solvent; ●, benzene plus 0.09 *M* 2,5-dimethyl-2,4-hexadiene; ◐, benzene plus 0.2 *M* *tert*-butyl alcohol; ▲, *tert*-butyl alcohol solvent.

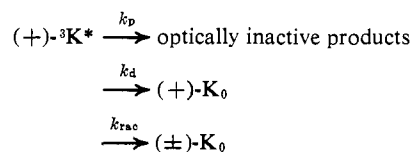
benzene are acetophenone (88%) and an unresolved mixture of *cis*- and *trans*-2-methyl-2-ethyl-1-phenyl-cyclobutanols (12%).

Irradiation of the ketone results in rapid loss of its optical activity. A 10-cm path of 0.10 *M* benzene solution produces an initial rotation of +0.198°. After 9% disappearance of ketone (as measured by glpc), the rotation of the solution is +0.120°; after 95% disappearance of ketone, the rotation is down to +0.006°; this value does not change upon further irradiation, while the last 5% of ketone disappears. After 16% conversion of a 0.10 *M* ketone solution in benzene, unreacted ketone was collected by preparative glpc and found to have undergone 31% racemization.

Since the final rotation of the ketone solutions was so close to zero, we could follow racemization of starting ketone quantitatively merely by comparing loss of activity of the photolyzed solution with disappearance of ketone (which leads to an almost inactive mixture of products). The observation of racemization of starting ketone demands an intermediate which can return to starting ketone and which lives long enough to lose chirality at the γ carbon. A 1,4 biradical is the most likely such intermediate. Nevertheless, for the sake of unprejudiced analysis, Scheme I makes no assumptions about mechanisms other than that racemization and product formation are competing processes originating from the triplet state.

Equation 1 (Appendix II) expresses the dependence of optical activity on ketone concentration $[K]$ in terms of Scheme I, where the subscript *i* indicates initial values. A plot of experimental results according to eq 1 in effect corrects for racemization of starting material, since Φ_{rac}^0/Φ_p equals the ratio of racemization/reaction

Scheme I



$$\log \frac{\alpha_i}{\alpha} = \left(1 + \frac{\Phi_{rac}^0}{\Phi_p} \right) \log \left(\frac{[K]_i}{[K]} \right) \quad (1)$$

$$\Phi_{rac}^0 = k_{rac}\tau_T \quad (2)$$

$$\Phi_p = k_p\tau_T = k_p(k_p + k_d + k_{rac})^{-1} \quad (3)$$

at zero conversion. This point is doubly important, because the results are independent of the optical purity of the starting material.

We irradiated several 0.1 *M* solutions of (*S*)-(+)-I to various conversions, with the results (see Experimental Section) plotted according to eq 1 in Figure 1. Table I summarizes the data. In benzene, the slope of 4 indi-

Table I. Quantum Yields for Photoreactions of (4*S*)-(+)-4-Methyl-1-phenyl-1-hexanone^a

Solvent	Φ_{Ir}^b	Φ_{cy}^c	Φ_{rac}^{0d}	Φ_{rac}/Φ_p^e
Benzene	0.23 ± 0.01	0.03	0.78 ± 0.05	3.0
Benzene + 0.09 <i>M</i> Q'	0.12 ± 0.005	0.015	0.39 ± 0.03	3.0
Benzene + 2% <i>t</i> -BuOH	0.32 ± 0.01	0.03	0.55 ± 0.05	1.6
<i>t</i> -BuOH	0.94 ± 0.01	0.05	0 ± 0.03 ^o	0.0

^a Degassed 0.10 *M* solutions irradiated at 3130 Å, 25°. ^b Acetophenone formation. ^c Cyclobutanol formation. ^d Racemization of starting material corrected to zero conversion. ^e Slope in Figure 1. ^f Q is 2,5-dimethyl-2,4-hexadiene, enough to quench half the reaction. ^o At 17% conversion.

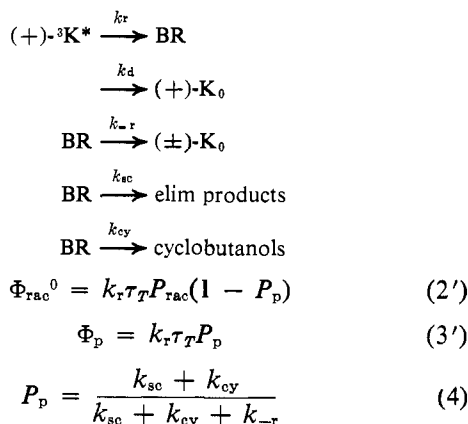
cates a Φ_{rac}^0/Φ_p ratio of 3. Since Φ_p is measured to equal 0.26, and since Φ_{isc} equals unity, $\Phi_{rac}^0 = 0.78$ and $\Phi_p + \Phi_{rac}^0 \approx 1$. In the presence of enough quencher to halve the quantum yield of product formation, the observed lack of any change in Φ_{rac}^0/Φ_p indicates the involvement of a single excited triplet. Every unquenched triplet must either react to yield product or undergo the reaction which produces racemization. The only reasonable mechanism for racemization is the expected γ -hydrogen abstraction yielding a 1,4 biradical which can rotate freely about the β,γ C-C bond before reverting to starting ketone.

A priori, the photoracemization of (+)-I might be analyzed as a competition between a concerted reaction leading to products and a γ -hydrogen abstraction leading to a biradical which only returns to racemized starting material. Apart from the unlikelihood of a 1,4 biradical not going on to products, the behavior of II and the observed solvent effects on quantum yields dictate against such a scheme. The increased product quantum yield in the presence of 2% *tert*-butyl alcohol is compensated for by a decreased quantum yield of racemization, $\Phi_p + \Phi_{rac}^0$ equalling 0.90. These observations, as well as Yang's recent work with aliphatic ketones,²² reaffirm our earlier observations and conclusions regarding solvent effects.⁶ In alcohol as solvent, the product quantum yield approaches unity and no racemization of starting material is observed. Con-

(22) N. C. Yang and S. P. Elliot, *J. Amer. Chem. Soc.*, **91**, 7550 (1969).

sequently we conclude that both racemization and product formation arise from the same biradical intermediate, which does not revert to starting ketone in the presence of sufficient alcohol. The unspecific Scheme I can be replaced with a specific mechanism (Scheme II)

Scheme II



in which $k_r \gg k_d$ ($k_r = 1/\tau_T$) for ketone I and P_{rac} is the percentage of biradical intermediates (BR) which lose chirality before reacting. Note that k_r replaces the hypothetical k_p in Scheme I.

The lack of ketone racemization in alcohol prompted us to look at the optical activity of the cyclobutanols formed under these conditions. The cyclobutanol mixture resulting from complete conversion of a 0.18 M solution of (+)-I in *tert*-butyl alcohol was collected by glpc and found to be levorotatory ($[\alpha]_{578}^{25} -0.19^\circ$, $[\alpha]_{546}^{25} -0.25^\circ$, $[\alpha]_{436}^{25} -0.32^\circ$, all $\pm 0.06^\circ$).

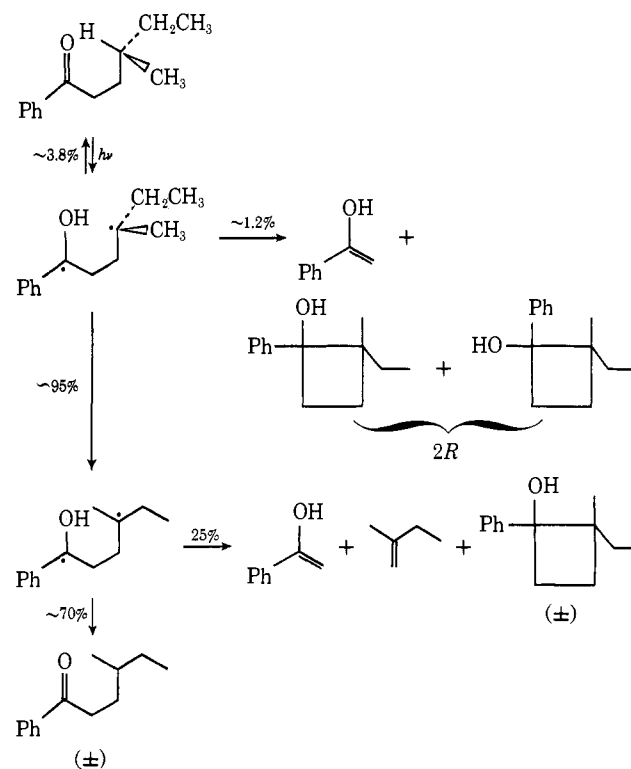
Comparison of all results where racemization occurs indicates an average ($\Phi_p + \Phi_{\text{rac}}^0$) value of 0.95 ± 0.05 . Although the value is within experimental error of unity, the small rotation observed in the cyclobutanol products probably indicates that the biradical intermediate is not quite long lived enough to completely lose its chirality through rotations about the β, γ C-C bond. P_{rac} might be estimated to equal 0.95. Until we can resolve the cyclobutanols and determine the actual degree of retention of configuration in their formation, we cannot determine the value of P_{rac} any more accurately.

Scheme III summarizes the most likely behavior of triplet I in benzene. In alcohol, re-formation of racemized ketone is suppressed.

Kinetic Consequences. The behavior of (+)-I indicates that its triplet lifetime is determined only by k_r , the rate of γ -hydrogen transfer. We have published a preliminary report of the total lack of any correlation between type II quantum yields and triplet state lifetimes for different ketones.²³ In contrast, triplet lifetimes decrease as expected with decreasing dissociation energy of the γ C-H bonds. We have concluded that the varying type II quantum yields of different ketones in hydrocarbon solvents must reflect different amounts of disproportionation of the different biradical intermediates back to ground state ketones. This conclusion is verified by the behavior of I. In fact, the kinetic results provide independent corroboration that k_d is negligible compared to k_r and that the quantum yields of type II reaction of most phenyl alkyl ketones do not reflect excited state reactivity. This statement holds

(23) P. J. Wagner and A. E. Kempainen, *J. Amer. Chem. Soc.*, **90**, 5896 (1968); **94**, 7495 (1972).

Scheme III



only when no other *chemical* reaction of the triplet competes with γ -hydrogen abstraction.

Deuterium Isotope Effect. Table II compares the

Table II. Deuterium Isotope Effect on Type II Reaction of Phenyl *n*-Octyl Ketone^a

Ketone	Φ_{II}^b	Φ_{max}^c	$k_q \tau, M^{-1}d$
$\gamma\text{-}h_2$	0.30	0.97	29
$\gamma\text{-}d_2$	0.31	0.85	87

^a 0.10 M benzene solutions irradiated at 3130 Å. ^b Total quantum yield for acetophenone and cyclobutanol formation in benzene. ^c Maximum quantum yields obtained upon addition of *tert*-butyl alcohol. ^d Stern-Volmer slopes with 2,5-dimethyl-2,4-hexadiene quencher.

behavior of nonanophenone- $\gamma\text{-}h_2$ and nonanophenone- $\gamma\text{-}d_2$. Deuteration at the γ position produces no change in quantum yield but increases the triplet lifetime by a factor of three, again indicating that quantum yields are independent of triplet reactivity. Correction for probable δ -hydrogen abstraction²⁴ and for incomplete deuteration indicates a k_H/k_D value of 4.8 for γ hydrogen abstraction. The following deuterium isotope effects have been reported for triplet photoelimination reactions: 7 for 2-hexanone,²⁵ 6 for 5-decanone,²⁶ 1.7 for γ -hydroxy- γ -phenylbutyrophenone,²⁷ and 2.7 for hydrogen abstraction from secondary alcohols by triplet benzophenone.²⁸ The isotope effect produced specifically by γ deuteration merely indicates the involvement of γ hydrogens. It is a necessary

(24) P. J. Wagner, P. A. Kelso, A. E. Kempainen, and R. G. Zepp, *ibid.*, **94**, 7500 (1972).

(25) D. R. Coulson and N. C. Yang, *ibid.*, **88**, 4511 (1966).

(26) A. Padwa and W. Bergmark, *Tetrahedron Lett.*, 5795 (1968).

(27) F. D. Lewis, *J. Amer. Chem. Soc.*, **92**, 5602 (1970).

(28) (a) W. M. Moore, G. S. Hammond, and R. P. Foss, *ibid.*, **83**, 2789 (1961); (b) W. M. Moore and M. D. Ketchum, *J. Phys. Chem.*, **68**, 214 (1964).

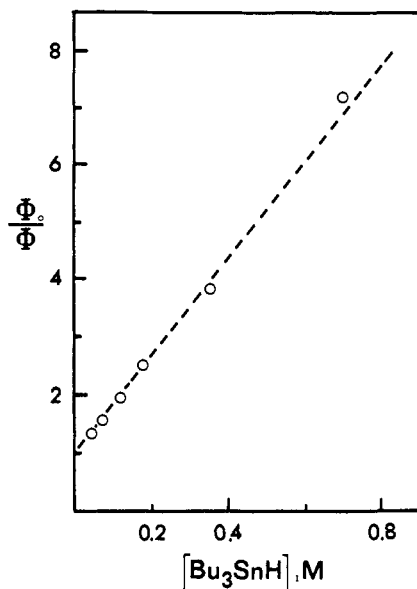


Figure 2. Quenching of acetophenone formation from valerophenone by tri-*n*-butylstannane in heptane. Dashed line is extrapolation of results from another run at stannane concentrations below 0.1 *M*.

condition, but not sufficient proof, of a biradical mechanism.

Biradical Trapping. Since stannanes and thiols have been used successfully to intercept free radicals which undergo rapid intramolecular processes,²⁹ we felt they might be able to trap the 1,4 biradical from valerophenone. Stannanes reduce ketone triplets very efficiently,³⁰ so any trapping of the intermediate biradical would yield a quadratic Stern-Volmer plot for the quenching of type II reaction by stannane. In fact we observe a linear Stern-Volmer plot (Figure 2) out to a

$$\frac{\Phi_{II}^0}{\Phi_{II}} = (1 + k_H[R_3SnH]\tau_T)(1 + k_H'[R_3SnH]\tau_{BR}) \quad (5)$$

Φ_0/Φ value of 7.3 (at 0.7 *M* stannane). The slope of 8.6 M^{-1} indicates a rate constant k_H of $1.1 \times 10^9 M^{-1} sec^{-1}$ for the reaction of triplet valerophenone with tributylstannane. The photoreduction of acetophenone by 0.38 *M* tributylstannane in heptane was quenched with naphthalene, yielding a $k_q\tau$ value of 19 M^{-1} and therefore a value of $1.3 \times 10^9 M^{-1} sec^{-1}$ for the rate constant for hydrogen abstraction from stannane by triplet acetophenone (based on $k_q = 1 \times 10^{10} M^{-1} sec^{-1}$).⁸

Low concentrations of thiols can enhance type II quantum yields,³¹ presumably acting similarly to alcohols. However, larger concentrations quench the reaction quite efficiently. Figure 3 shows how dodecyl mercaptan quenches acetophenone formation from γ -methoxybutyrophenone (γ -MOB) in benzene containing 1.2 *M* pyridine, under which conditions the unquenched quantum yield is close to unity. Dodecyl mercaptan quenches the type II reaction of valerophenone and butanethiol quenches γ -MOB in 2 *M* *tert*-butyl alcohol just as efficiently ($k_q\tau = 1.8 M^{-1}$); butanethiol-*S-d*₁ quenches only one-third as efficiently. In order to determine how much of the type II quenching by thiols

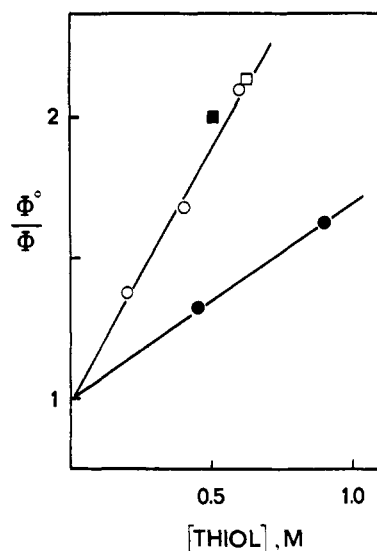


Figure 3. Quenching of type II reactions by thiols in benzene containing pyridine: \circ , dodecyl mercaptan and γ -methoxybutyrophenone; \square , dodecyl mercaptan and valerophenone; \bullet , butanethiol-*S-d*₁ and γ -methoxyvalerophenone (another Φ_0/Φ value of 2.8 at 2.8 *M* thiol); \blacksquare , butanethiol and γ -methoxyvalerophenone in benzene containing 2 *M* *tert*-butyl alcohol.

involves triplet ketone, we compared the efficiencies with which 2,5-dimethyl-2,4-hexadiene, butanethiol, and butanethiol-*S-d*₁ quench the phosphorescence of acetophenone in degassed benzene. Measured $k_q\tau_T$ values are 26,000, 78, and 73 M^{-1} , respectively.³² Since k_q for the diene is assumed to be equal to $5 \times 10^9 M^{-1} sec^{-1}$,⁸ k_q for both thiols is $1.4 \times 10^7 M^{-1} sec^{-1}$.

Thiol quenching of the type II reaction represents biradical trapping for the following kinetic reasons. First, the equal $k_q\tau$ values toward both valerophenone and γ -MOB cannot represent triplet quenching, since the triplet lifetimes of these two ketones differ by a factor of five.²³ Second, the measured k_q value of thiols toward triplet acetophenone predicts $k_q\tau_T$ values of only 0.11 and 0.02 M^{-1} toward the two photoeliminating ketones instead of the $k_q\tau$ value of 1.8 M^{-1} actually observed. Third, phosphorescence quenching is subject to no deuterium isotope effect, whereas type II quenching is subject to a threefold effect.

Thiols apparently quench acetophenone triplet by a charge-transfer process,^{32,33} while their quenching of the type II reaction clearly suggests alkyl radical-like abstraction of hydrogen from sulfur.

A benzene solution 0.2 *M* in γ -MOB and 3.7 *M* in butanethiol-*S-d*₁ was irradiated at wavelengths greater than 330 nm such that about 0.2 einstein/l. was absorbed. Unreacted ketone was collected by preparative vpc and subjected to nmr and mass spectral analysis, both of which indicated that specifically the γ position was 33% deuterated. In the mass spectrum, the 50% (46 + 47)/45 *m/e* ratio corresponding to the CH_3OCH_2 cation (β,γ C-C cleavage facilitated by oxygen) attested to the specificity of deuterium incorporation at the γ position. Likewise, the intensity of the nmr absorption of the γ -methylene at δ 3.2 was lower than that

(32) R. G. Zepp and P. J. Wagner, *Chem. Commun.*, 167 (1972).

(33) (a) J. B. Gutenplan and S. G. Cohen, *Chem. Commun.*, 247 (1969); (b) A. Padwa and A. Battisti, *J. Amer. Chem. Soc.*, 93, 1305 (1971).

(29) H. G. Kuivila, *Accounts Chem. Res.*, 1, 299 (1968).

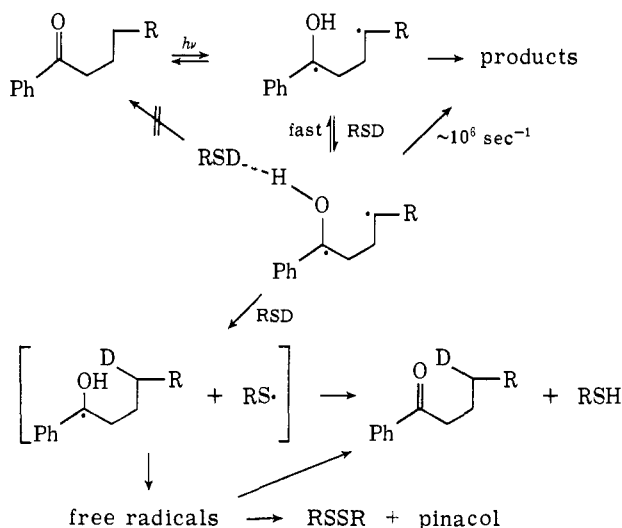
(30) P. J. Wagner, *J. Amer. Chem. Soc.*, 89, 2503 (1967).

(31) P. J. Wagner and J. M. McGrath, *ibid.*, 94, 3849 (1972).

displayed by unirradiated ketone. The efficient γ deuteration of γ -MOB establishes that the γ -radical site of the 1,4-biradical intermediate attacks thiol at a rate competitive with the usual intramolecular biradical reactions.

A quantitative labeling experiment was performed by irradiating a benzene solution containing 0.2 M γ -MOB and 2.7 M butanethiol-*S-d* to 20% conversion, with the following quantum yields being measured: loss of ketone, 0.57; acetophenone, 0.27; cyclobutanols, 0.07; butyl disulfide, 0.11; γ -MOB- γ -*d*₁, 0.33. The formation of disulfide suggests that the pinacol derived from starting ketone was also formed. In fact a compound assumed to be the pinacol did crystallize out of large-scale photosylates, but we did not characterize it or analyze for it quantitatively. None of the reduction product 1-phenyl-4-methoxy-1-butanol was detected, nor was any other product, the thiol trapping being a very clean reaction. If it is assumed that just as much pinacol as disulfide is formed, no other products being observed, the results indicate a 100% material balance. The trapping experiment indicated that 56% of the biradicals attacked 2.7 M deuteriothiol, in good agreement with the quenching experiment which indicates 63% quenching.

Based simply on our kinetic product observations, we can construct the following scheme for photointeractions of thiols with ketones which normally undergo type II photoprocesses.



Biradical Lifetimes. From the $k_q\tau_{BR}$ value indicated in Figure 3, it should be possible to make a very good estimate of τ_{BR} by assuming that k_q equals the rate of hydrogen abstraction from thiols by alkyl radicals. The literature abounds with such numbers, but unfortunately they vary tremendously, values of $\sim 10^5$, $\sim 10^6$, and $\sim 10^8 \text{ M}^{-1} \text{ sec}^{-1}$ being reported.³⁴⁻³⁶ Since thiols and trialkylstannanes show similar efficiencies in intercepting radicals which undergo rapid intramolecular rearrangements,^{37,38} and since stannanes are re-

ported to trap alkyl radicals with rate constants $10^6 \text{ M}^{-1} \text{ sec}^{-1}$,³⁸ we tentatively estimate τ_{BR} for the *solvated* biradicals from valerophenone and γ -MOB to be $\sim 10^{-6} \text{ sec}$.

The lack of significant curvature in Figure 2 indicates a maximum $\tau_{BR} < 2 \times 10^{-7} \text{ sec}$ for the *unsolvated* biradical from valerophenone, again based on the assumption that k_H' in eq 5 is $10^6 \text{ M}^{-1} \text{ sec}^{-1}$. Of course, a solvated biradical should be appreciably longer lived than the unsolvated biradical, since solvation eliminates the major reaction of free biradical and slows down cyclization.⁶ Consequently, a $\tau_{BR} \sim 10^{-7} \text{ sec}$ for unsolvated biradical is not an unreasonable estimate when compared to the τ_{BR} estimated from thiol trapping of solvated biradical.

Spin Considerations. Triplets I²³ and II²⁰ react with their γ C-H bonds at the same rate, $4 \times 10^8 \text{ sec}^{-1}$. Since tertiary aliphatic and secondary benzylic C-H bonds generally have similar reactivities toward radical reagents,³⁹ the equal reactivity of the two ketone triplets would be expected if they both react by γ -hydrogen atom abstraction. Any concerted elimination from triplet II should in fact manifest itself as an enhanced rate relative to that displayed by triplet I. The maximum rate for concerted elimination of triplet II can be no faster than $4 \times 10^6 \text{ sec}^{-1}$. We have argued that such a concerted elimination would be thermoneutral or somewhat exothermic, and we might seek some rationalization for its sluggishness. Given the uncertainties in the thermochemical estimates, it is possible that a concerted elimination would be a few kilocalories endothermic, especially if twisted triplet stilbene is not much more stable than triplet *trans*-stilbene. In this regard our recent finding that triplet energies of phenyl alkyl ketones in solution are 2.5 kcal lower¹² than the well-known 74.5-kcal value observed in glasses⁴⁰ tends to diminish slightly the certitude of our original¹⁹ conclusions. Nonetheless, since we tried to estimate *minimum* values for exothermicities, it is likely that triplet II does have enough energy to yield triplet stilbene but that the concerted reaction is slowed by steric constraints or poor orbital overlap. In particular, the planar transition state favored by MO calculations⁴¹ is subject to considerable eclipsing about the C_α - C_β bond and would produce an enol with a 90° twisted double bond. Such a twisted enol would have to be formed as a triplet, for which there is insufficient energy.

Of course, spin inversion must occur somewhere during these triplet state reactions. A biradical probably offers this system—and most triplet systems—the easiest path for doing so. Triplet ketone can proceed smoothly to triplet biradical. Spin-spin interactions in a 1,4 biradical are probably so weak that $T \leftrightarrow S$ interconversions would then be very rapid. In fact, the relatively long biradical lifetimes which we have estimated most likely are determined exclusively by activation barriers to their chemical reactions, as suggested by Stephenson and Braumann,⁴² with spin inversion taking place in no more than 1 nsec. Biradical lifetimes will be

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(35) (a) C. Sivertz, *J. Phys. Chem.*, **63**, 34 (1959); (b) R. D. Burkhart, *ibid.*, **73**, 2703 (1969).

(36) B. Smaller, J. R. Remko, and E. C. Avery, *J. Chem. Phys.*, **48**, 5174 (1968).

(37) (a) C. Walling and M. S. Pearson, *J. Amer. Chem. Soc.*, **86**, 2262 (1964); (b) C. Walling, J. H. Cooley, A. A. Ponaras, and E. J. Rauch, *ibid.*, **88**, 5361 (1966).

(38) D. J. Carlson and K. U. Ingold, *ibid.*, **90**, 1055, 7047 (1968).

(39) C. Walling and M. Mintz, *ibid.*, **89**, 1515 (1967).

(40) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *ibid.*, **86**, 4537 (1964).

(41) F. P. Boer, T. W. Shannon, and F. W. McLafferty, *ibid.*, **90**, 7239 (1968).

(42) L. M. Stephenson and J. I. Braumann, *ibid.*, **93**, 1988 (1971).

discussed at greater length in a separate paper concerning various aspects of biradical behavior.

Summary

The lack of triplet stilbene formation in the triplet state type II photoelimination of β,γ -diphenylbutyrophenone indicates that the reaction does not proceed concertedly even when energetically it probably could. The total of quantum yields for type II processes and for photoracemization of (4S)-(+)-4-methyl-1-phenyl-1-hexanone is very close to unity. This experiment establishes several facts. There exists an intermediate which can lose its configurational integrity at the γ carbon, which lives long enough to do so almost completely, and which can return to the ground state of ketone; this intermediate is formed in 100% efficiency from the triplet, in accord with our various suggestions based on solvent effects⁶ and kinetic studies²³ that n,π^* triplet ketones undergo no direct physical decay. The 1,4-biradical nature of the intermediate is evidenced by its behavior as well as by its rate of formation.²³ Thiol trapping suggests typical biradical lifetimes of 10^{-6} – 10^{-7} sec.

Experimental Section

Materials. Commercial thiophene-free benzene was washed with sulfuric acid until no further coloration of the acid layer took place. Then the benzene was washed with water and distilled from phosphorus pentoxide. Reagent grade *tert*-butyl alcohol was distilled from sodium. *n*-Tetradecane was purified in the same manner as benzene, while *n*-eicosane was recrystallized from ethanol and dried *in vacuo*. Commercial *cis*-stilbene (Aldrich) and commercial *trans*-stilbene (Eastman) were used as received. 2,5-Dimethyl-2,4-hexadiene (Chemical Samples) sublimed to the top of the bottle in a refrigerator and the resulting crystals were used as such. Valerophenone (Aldrich) was recrystallized from pentane, passed through neutral alumina, and finally distilled at reduced pressure. Thiols were distilled or recrystallized commercial materials. Deuteriothiol (95% d_1 by nmr analysis) was prepared by two equilibrations of butanethiol in tenfold excesses of D_2O .

γ -Methoxybutyrophenone was prepared as described elsewhere.²³

β,γ -Diphenylbutyrophenone¹⁷ was prepared by the addition of chalcone to benzyl magnesium chloride and a catalytic amount of cuprous chloride in anhydrous ether at 5°, followed by addition of the reaction mixture to an excess of a cold vigorously stirred saturated ammonium chloride solution. The white crystalline ketone was collected by filtration, recrystallized three times from ethanol, and dried *in vacuo* mp (uncorrected) 115° (lit.¹⁷ 113°).

4-Methyl-1-phenyl-1-hexanone was prepared in a manner similar to the procedure employed by Shaikh and Thakar⁴³ from (S)-(-)-2-methyl-1-butanol (Aldrich), $[\alpha]_D^{25}$ (neat) -5.80° . Crude 2-methyl-1-butyl tosylate, prepared by the addition of tosyl chloride to the alcohol in pyridine, was added dropwise to an ice-cooled solution of 1 equiv of sodium and 2 equiv of diethyl malonate in absolute ethanol. The solution was allowed to warm to room temperature and was then refluxed for 5 hr. After the ethanol was removed, the reaction mixture was quenched with water and extracted with ether. The crude α -amylmalonic ester, bp 91° (2 mm), obtained from the distillation of the ether extract was refluxed for 2 hr with concentrated aqueous KOH. The cooled solution was treated with H_2SO_4 and refluxed for 7 hr. The mixture was extracted repeatedly with ether. The ether extract was dried over magnesium sulfate and distilled. The crude 3-methylpentanoic acid, bp 90° (2 mm), was treated with a 20% excess of freshly distilled thionyl chloride at 0°. The reaction mixture was stirred overnight at room temperature. The thionyl chloride was removed by vacuum distillation and anhydrous benzene was added. Anhydrous aluminum chloride (1 equiv) was added in portions to the ice-cooled benzene solution. The mixture was stirred at room temperature for 7 hr and treated with HCl in ice and extracted with

benzene. The benzene extract was dried ($MgSO_4$), distilled (bp 89° (0.6 mm)), and chromatographed on alumina to yield pure (S)-(+)-I.

Nonanophenone (Eastman) was distilled at reduced pressure, recrystallized from pentane, and chromatographed on alumina. Nonanophenone- γ - d_8 , bp 140–141° (3 mm), was prepared from acetophenone and the tosylate of 1-heptanol-2,2- d_8 by the general method of Stork and Dowd.⁴⁴ The cyclohexylimine of acetophenone was added to ethyl magnesium bromide in tetrahydrofuran. After the solution was refluxed for 4 hr and then cooled to 0°, the tosylate was added with stirring. The solution was allowed to warm to room temperature and was stirred overnight. The reaction mixture was then refluxed for 3 hr with an excess of 10% hydrochloric acid, cooled, and extracted with chloroform. The chloroform abstracts were dried and distilled. Material boiling at 100–150° at 0.6 Torr was collected and shown to be a mixture of nonanophenone and β -phenylbutyrophenone. The nonanophenone was isolated and purified by another distillation, repeated low-temperature recrystallization from pentane, and chromatography on neutral alumina. Mass spectral analysis indicated that the ketone was 84% d_8 , 14% d_1 , and 2% d_0 at the γ position. The deuterated heptanol, bp 91–92° (25 mm), was prepared by lithium aluminum hydride reduction of heptanal-2,2- d_8 , which was prepared by refluxing heptanal (Eastman) for 4 hr in excess D_2O containing enough potassium carbonate to give pH 11. The partially deuterated aldehyde was extracted into ether and treated three more times with D_2O . Nmr analysis of the heptanal indicated >95% deuteration and we do not know why the ketone was incompletely deuterated.

All ketones were >99.5% pure by glpc analysis and were identified by their nmr and mass spectra.

Preparation of Samples for Irradiation. Solutions containing known concentrations of ketone, internal standard(s), and any other additives were prepared in volumetric flasks. Then 3.0-ml portions of these solutions were syringed into separate, constricted, 100 × 13 mm Pyrex culture tubes. The samples were degassed by three freeze-pump-thaw cycles and sealed *in vacuo* at ≤ 0.005 Torr.

Irradiation of Samples. Irradiations were performed in a "merry-go-round" apparatus⁴⁵ with a Hanovia 450-W medium-pressure mercury lamp contained in a water-cooled, quartz immersion well. Corning No. 7-83 filter combinations were used to isolate the 3600-Å line and a 1-cm path of 0.002 M potassium chromate in 5% aqueous potassium carbonate was used to isolate the 3025–3130-Å lines. The entire apparatus was immersed in a water bath. The "merry-go-round" ensures that the same intensity of radiation impinges on each sample of a set of simultaneously irradiated samples.

Quantum Yields. All quantum yields for the formation of acetophenone were determined relative to the formation of acetophenone from valerophenone in benzene on parallel irradiation of samples of identical volumes and concentrations. The quantum yield of acetophenone formation has been determined to be 0.33 for 0.10 M valerophenone in benzene.²³ Conversion of valerophenone was limited to 6%. Quantum yields for cyclobutanol formation and/or ketone disappearance were determined relative to the quantum yield of acetophenone formation for I and II.

Quantitative Analysis. All analyses for product formation and/or starting ketone disappearance were performed on an Aero-graph Model 1200 gas chromatograph with a 9 ft × 1/8 in. column fitted for on-column injection and containing 4% QF-1 and 1% Carbowax 20M on 60–80 mesh Chromosorb G. The area ratios of the starting materials and/or products to the appropriate internal standard(s) (*n*-tetradecane or *n*-eicosane) were measured on a L&N Model H recorder fitted with a disk integrator. The area ratios were converted to mole ratios by calibration with known mixtures.

Determination of Optical Rotations. All optical rotations were measured on 6-ml samples with a Perkin-Elmer Model 141 automatic polarimeter. The rotation of the 0.10 M (+)-I samples was obtained before degassing. For a given run, irradiation of a number of identical samples was begun simultaneously. Sets of two or four tubes were removed at intervals. The contents of two tubes were combined and their optical rotation measured. The solutions were then analyzed for ketone disappearance and for acetophenone formation. Table III contains the results observed

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(45) F. G. Moses, R. S. H. Liu, and B. M. Monroe, *Mol. Photochem.*, **1**, 245 (1969).

(43) A. A. Shaikh and K. A. Thakar, *J. Indian Chem. Soc.*, **43**, 340 (1966).

Table III. Optical Activity of Solutions of (*S*)-(+)-4-Methyl-1-phenyl-1-hexanone as a Function of Conversion

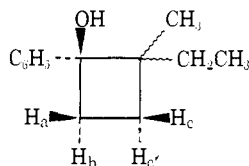
[K], <i>M</i>	$[\alpha]^{25D}$	% conversion
Solvent = Benzene		
0.0944	+0.176	0
0.0900	+0.144	4.7
0.0856	+0.120	9.3
0.0824	+0.102	12.6
0.0794	+0.088	15.9
0.0754	+0.071	20.2
0.0011	+0.006	99.9
Solvent = Benzene + 0.09 <i>M</i> Diene		
0.1016	+0.190	0
0.0971	+0.156	4.5
0.0900	+0.116	11.4
0.0863	+0.106	15.0
Solvent = Benzene + 0.02 <i>M</i> <i>tert</i> -Butyl Alcohol		
0.0981	0.182	0
0.0886	0.142	9.7
0.0853	0.124	13.1
0.0835	0.119	14.9
0.0804	0.110	18.0
Solvent = <i>tert</i> -Butyl Alcohol		
0.102	0.220	0
0.085	0.181	17.2

in different runs. Rates of ketone disappearance were zero order with time.

After 16% conversion of 12 ml of 0.1 *M* (+)-I in benzene, 0.05 g of unreacted ketone was collected by preparative glpc on a Hewlett-Packard Model 776 with a 20 ft \times $\frac{3}{8}$ in. column packed with 4% QF-1 and 1% Carbowax 20M on 30-60 mesh support. The weighed ketone was transferred quantitatively to a 10-ml volumetric flask and diluted to volume with benzene. The resulting solution exhibited a rotation of +0.034° at 589 and 578 nm.

Isolation of Cyclobutanols. After >99% conversion of 25 ml of 0.2 *M* (+)-I in *tert*-butyl alcohol, solvent was removed and the residue chromatographed on neutral alumina. The cyclobutanol-rich fraction yielded 0.093 g of a mixture of the isomeric cyclobutanols after preparative glpc (see above). The product was dissolved in 6 ml of benzene and displayed the following optical rotations: -0.003° at 589 and 578 nm, -0.004° at 546 nm, -0.005° at 436 nm. The precision of all readings was $\pm 0.001^\circ$. The measured rotation of a blank (cell filled with benzene) was $0 \pm 0.001^\circ$.

That the isolated product was indeed the expected cyclobutanol mixture was demonstrated by the hydroxyl peaks and lack of carbonyl peaks in its ir spectrum and by the following nmr spectrum (CCl₄-TMS): δ 7.25 (br s, 5 H, C₆H₅), 2.6 (m, 1 H, H_a), 2.18 (s, 1 H, OH), 1.2-2.2 (overlapping signals, 5 H, H_b, H_c, CH₂CH₃), 0.58 and 1.13 (2 s, total 3 H, ring methyls of two diastereomers), 0.89 (t, 3 H, CH₂CH₃). The ratio of the δ 0.58 and 1.13 singlets indicated almost equal amounts of the two diastereomers.



Quenching of Valerophenone by Stannane. Heptane solutions containing 0.10 *M* valerophenone, 0.005 *M* octadecane, and various concentrations of tri-*n*-butylstannane (0-0.7 *M*) were prepared. Three milliliters of each sample was placed in each of two Pyrex tubes, which were then all degassed in three freeze-pump-thaw cycles, sealed, and irradiated in parallel at 3130 Å. Vpc analysis of product formation in solutions containing 0.7 *M* stannane indicated quantum yields for formation of 1-phenyl-1-pentanol and acetophenone of 0.90 and 0.04, respectively. At lower concentrations of stannane, the combined yields of these products and cyclobutanols did not account completely for ketone disappearance, presumably because of competing pinacol formation.

Quenching of Stannane Photoreduction of Acetophenone. Similarly prepared heptane solutions containing 0.10 *M* acetophenone, 0.38 *M* stannane, and various concentrations of naphthalene were

irradiated in parallel at 3130 Å. Disappearance of ketone was monitored by uv analysis of the solutions.

Quenching of Photoelimination by Thiols. Benzene solutions 0.1 *M* in ketone, 1.2 *M* in pyridine, 0.0063 *M* in tetradecane, and containing various concentrations of *n*-dodecyl mercaptan (Aldrich), butanethiol (Eastman) or butanethiol-*S-d* were prepared, degassed, irradiated, and analyzed as usual. The butyl disulfide elutes from the usual QF-1-Carbowax vpc column just before tetradecane.

Quenching of Phosphorescence by Thiols. Benzene solutions 0.0056 *M* in acetophenone and containing various concentrations of butanethiol, butanethiol-*S-d* (0.01-0.03 *M*), or 2,5-dimethyl-2,4-hexadiene ($3-6 \times 10^{-5}$ *M*) were prepared as usual, placed in 13 \times 100 mm Pyrex tubes, and degassed very thoroughly. Acetophenone phosphorescence was induced with 313-nm excitation on an Aminco-Bowman spectrophotofluorometer. Phosphorescence intensities at 420 nm were read directly off the microphotometer for the quenching studies. After each degassed sample was measured, the tube was opened. The emission intensity of the aerated sample was subtracted from the original intensity reading to correct for impurity or byproduct fluorescence.

Labeling with Butanethiol-*S-d*. A degassed Pyrex tube containing 3 ml of a benzene solution 0.2 *M* in γ -MOB and 3.7 *M* in C₄H₉SD was attached to the outside well of a standard immersion well fitted with a 450-W Hanovia mercury arc filtered only by a uranium glass sleeve. The solution was irradiated for 3 hr. Unreacted γ -MOB was collected by preparative vpc and analyzed spectroscopically for deuterium incorporation: ir, br weak band 2100 cm⁻¹; nmr δ 3.2 (m, ~1 H, CHDO; t, 2 H in normal γ -MOB), 7.2-7.8 (m, 5 H, C₆H₅), 3.1 (s, 3 H, OCH₃), 2.8 (t, 2 H, CH₂C=O), 1.75 (m, 2 H, middle CH₂); 70-eV mass spectrum, following *m/e* ratios equalled 0.5, after correction for ¹³C: (179 + 180)/178; 121/120; (46 + 47)/45.

Three samples 2.7 *M* in C₄H₉SD were irradiated at 313 nm on a merry-go-round in parallel with a valerophenone actinometer. One identical sample was kept in the dark. Yields of product formation (0.024 *M*) and ketone disappearance (0.040 *M*) were determined by vpc analysis. The actinometer indicated $I_a = 0.070$ einstein/l. Unreacted γ -MOB was collected by preparative vpc from both photolyzed and unphotolyzed samples. The mass spectrum of the unphotolyzed blank showed only ¹³C isotopes at *m/e* 179, 121, and 46, whereas the photolyzed ketone displayed 121/120 and 46/45 *m/e* ratios of 12%.

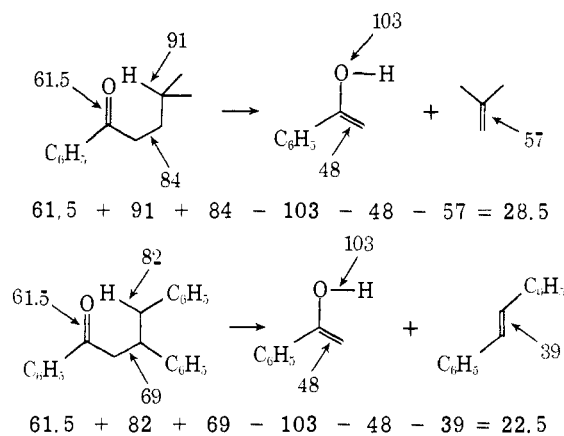
Acknowledgment. This work was supported by grants from the National Science Foundation.

Appendix I

Thermochemical Estimates. Since our estimate of the exothermicity of the type II photoelimination of II indicates that a concerted reaction would be very close to thermoneutral, we describe below the exact figures and assumptions upon which our estimates are based.

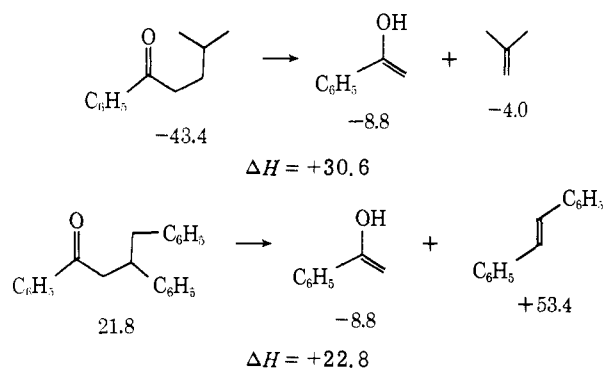
We have calculated ΔH for the cleavage of I and II in two ways: (1) by consideration of dissociation energies of the bonds being broken and being formed; (2) from heats of formation of reactants and products.

The following two pictures indicate the bond energies in kcal/mol



Values for C-H, O-H, and C-C bonds are standard.⁴⁶ Values for π bonds were calculated from known⁴⁷ heats of formation of the olefin and its hydrogenated derivative: $D_\pi = \Delta H_f(\text{RCH}_2\text{CH}_2\text{R}') - D(\text{H-H}) + D(\text{RCH}_2\text{CHR}'\text{-H}) + D(\text{R}'\text{CH}_2\text{CHR-H}) - \Delta H_f(\text{RCH=CHR}')$; $D_\pi(\text{CH}_2=\text{C}(\text{CH}_3)_2) = -32.2 - 104 + 98 + 91 + 4.0 = 57$; $D_\pi(\text{C}_6\text{H}_5\text{CH=CHC}_6\text{H}_5) = +32.4 - 104 + 82 + 82 - 53.4 = 39$; $D_\pi(\text{C}_6\text{H}_5\text{C}(\text{CH}_3)=\text{CH}_2) = +0.9 - 104 + 98 + 80 - 27 = 48$; $D_\pi(\text{C}_6\text{H}_5\text{CH=O}) = -22.5 - 104 + 103 + 79 + 6 = 61.5$. We are assuming that the carbonyl π -bond strength in the phenyl alkyl ketones is the same as in benzaldehyde; the π -bond strengths of olefins generally are not changed by alkoxy substituents.⁴⁷ Values for benzylic C-H bond strengths must be assumed; we have proceeded on the basis that α substituents lower benzylic C-H bond strengths by three-fourths the amount they lower the C-H bond strength of ethane.

Heats of formation of isobutylene⁴⁷ and stilbene⁴⁸ are known. The others were calculated by Benson's method.⁴⁷



The entropy change both for 1-pentene going to 1-propylene plus ethylene and for 2-pentanone going to acetone plus ethylene is +30 eu⁴⁷ and we assume that a similar value will apply to most type II eliminations.

It is interesting to compare a few of the calculated bond energies and heats of formation with relevant experimental facts. For example, our calculated

(46) J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966).

(47) S. W. Benson, *et al.*, *ibid.*, **69**, 279 (1969).

(48) S. Marantz and G. T. Armstrong, *J. Chem. Eng. Data*, **13**, 599 (1968).

ΔH_f for acetophenone enol is 13 kcal higher than the known ΔH_f for acetophenone itself,⁴⁷ whereas the measured values in solution are 7 kcal for acetone and ~ 5 kcal for acetophenone.^{49,50} Likewise, the activation energy for thermal cis-trans isomerization of stilbene⁵¹ suggests a minimum π -bond energy of 48 kcal for *trans*-stilbene. Therefore, our estimates very likely provide *minimum* values for the exothermicity of triplet ketones undergoing type II cleavage.

Appendix II

Derivation of Equation 1. Application of the steady-state treatment to Scheme I yields the following expressions, where [K] is the total ketone concentration.

$$[(+)\text{-K}^*] = \frac{[(+)\text{-K}]}{[K]} I\tau_T \quad (6)$$

$$[(+)\text{-K}^*] + [(+)\text{-K}^*] = I\tau_T \quad (7)$$

$$-\frac{d[K]}{dt} = k_p I\tau_T \quad (8)$$

$$-\frac{d[(+)\text{-K}]}{dt} = (k_p + k_{\text{rac}}) \frac{[(+)\text{-K}]}{[K]} I\tau_T \quad (9)$$

The optical activity of the solution is directly proportional to the concentration of the unracemized enantiomer.

$$\alpha = S[(+)\text{-K}] \quad (10)$$

$$\frac{d\alpha}{dt} = \frac{Sd[(+)\text{-K}]}{dt} \quad (11)$$

$$\frac{d\alpha}{dt} = \frac{-S(k_p + k_{\text{rac}})[(+)\text{-K}]I\tau_T}{[K]} \quad (12)$$

Substitution of the equalities expressed in eq 8 and 10 into eq 12, followed by slight rearrangement, yields

$$\frac{d\alpha}{\alpha} = \left(\frac{k_p + k_{\text{rac}}}{k_p} \right) \frac{d[K]}{[K]} \quad (13)$$

Integration yields eq 14 which is equivalent to 1.

$$\log \left(\frac{\alpha_i}{\alpha} \right) = \left(1 + \frac{k_{\text{rac}}}{k_p} \right) \log \left(\frac{[K]_i}{[K]} \right) \quad (14)$$

(49) A. Gero, *J. Org. Chem.*, **19**, 1960 (1954).

(50) S. Sunner, *Acta Chem. Scand.*, **11**, 1757 (1960).

(51) P. Bortolus and G. Cauzzo, *Trans. Faraday Soc.*, **66**, 1161 (1970).