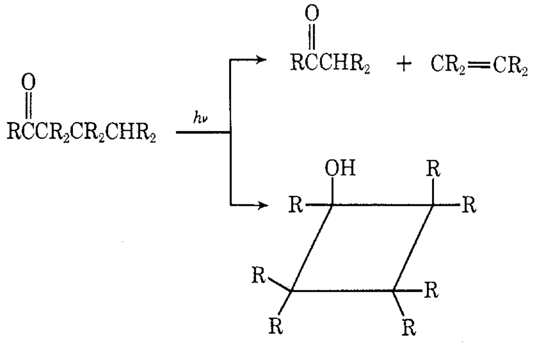
Type II Photoelimination and Photocyclization of Ketones

PETER J. WAGNER
Department of Chemistry, Michigan State University, East Lansing, Michigan

Received October 5, 1970

Despite the intense activity in organic photochemistry in the past decade, few photoreactions have been subjected to mechanistic scrutiny in anywhere near the detail applied to most ground-state reactions. In fact, photochemists do ask many mechanistic questions identical with those asked by ground-state chemists. (How do structural variations affect reactivity? Are there any intermediates involved?) These kinds of questions have not been answered in any systematic way for most photoreactions, primarily because they cannot be answered satisfactorily until some questions unique to excited-state chemistry are answered. (Which state(s) reacted? How did excited states which did not react return to the ground state?) It therefore seems desirable to summarize recent research on a photoreaction about which most of the fundamental mechanistic questions unique to photochemistry as well as many of those shared with ground-state chemistry can now be answered.

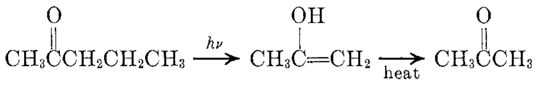
Carbonyl compounds containing γ C–H bonds undergo, upon electronic excitation, characteristic 1,5-hydrogen shifts to yield both cleavage and cyclization products. The reactions have been studied most extensively with ketones. The cleavage reaction is commonly called Norrish type II photoelimination, after its discoverer.[1] Cyclobutanol formation, which almost always accompanies cleavage, was first reported by Yang in 1958.[2] I shall call them together the type II photoprocesses.



These reactions have been of widespread mechanistic interest because they are induced by all forms of electronic excitation, including γ rays and electron impact. In the latter category, the McLafferty rearrangement[3] is the well-known mass spectral analog of type II photoelimination. The reactions are also of practical interest. The synthetic potential for making otherwise unobtainable cyclobutane derivatives is enormous. Much of the photodegradation of polyethylene-like polymers is thought to be caused by type II elimination. In fact, serious studies are under way of the feasibility of copolymerization with carbon monoxide as a means of introducing controlled photodegradability into otherwise inert polymers.[4]

1,5-Hydrogen Transfer

Both the elimination and cyclization reactions involve transfer of a hydrogen from the γ carbon to the carbonyl oxygen. Although a ketone is the product isolated from type II elimination, it is preceded by the corresponding enol. Infrared monitoring of the photolysis of gaseous 2-pentanone revealed the formation of propen-2-ol which then slowly changed to acetone itself.[5]



$$\mathrm{CH_3\overset{\overset{O}{\|}}{C}CH_2CH_2CH_3 \xrightarrow{h\nu} CH_3\overset{\overset{OH}{|}}{C}{=}CH_2 \xrightarrow[heat]{} CH_3\overset{\overset{O}{\|}}{C}CH_3}$$

The specific involvement of a γ hydrogen was established by the observation of some acetone-d_1 in the photolysis of 2-hexanone-5-d_2[6] and by the large isotope effect on excited-state lifetimes produced specifically by γ deuteration.[7]

Identity of Reactive Excited-State Multiplicity

With aliphatic ketones, it is now well established that both singlet and triplet n,π* states undergo type II elimination.[7-9] The evidence is that only part of the reaction can be quenched by conjugated dienes, which are very efficient triplet quenchers but inefficient singlet quenchers. The percentage of singlet reaction depends on the γ C–H bond strength. Thus 2-pentanone (D = 98 kcal/mole) reacts mostly from the triplet, 5-methyl-2-hexanone (D = 91 kcal/mole) mostly from the singlet, and 2-hexanone (D = 94.5 kcal/mole) about equally from both states. Ignorance of this structure–reactivity trend caused considerable confusion in the early literature.

Cyclobutanol formation from aliphatic ketones occurs mostly from the triplet state,[7,9] which fact is evidenced by significant decreases in the ratio of cyclization to elimination products with increasing concentrations of triplet quencher.

---

(1) R. G. W. Norrish, *Trans. Faraday Soc.*, **33**, 1521 (1937).

(2) N. C. Yang and D.-H. Yang, *J. Amer. Chem. Soc.*, **80**, 2913 (1958).

(3) F. W. McLafferty, *Anal. Chem.*, **28**, 306 (1956); **31**, 82 (1959).

(4) G. H. Hartley and J. E. Guillet, *Macromolecules*, **1**, 165, 413 (1968).

(5) G. R. McMillan, J. G. Calvert, and J. N. Pitts, Jr., *J. Amer. Chem. Soc.*, **86**, 3602 (1964).

(6) R. Srinivasan, *ibid.*, **81**, 5061 (1959).

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

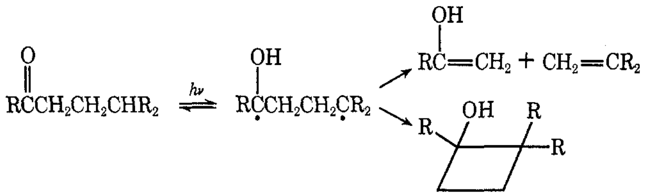
(8) P. J. Wagner and G. S. Hammond, *ibid.*, **87**, 4009 (1965); T. J. Dougherty, *ibid.*, **87**, 4111 (1965).

(9) (a) N. C. Yang, S. P. Elliot, and B. Kim, *ibid.*, **91**, 7551 (1969); (b) N. C. Yang and S. P. Elliot, *ibid.*, **91**, 7550 (1969).

With aromatic ketones, where intersystem crossing yields are generally unity, both reactions occur only from triplet states.[10] For example, at 4 M pentadiene in pentane, where 99.2% of the photoelimination of γ-phenylbutyrophenone has been quenched, the Stern–Volmer quenching plot is still linear.[11] In diene as solvent, 99.5% of the reaction is quenched.[11] It is not possible to distinguish whether the residual reaction comes from a small amount of singlet reaction competing with intersystem crossing or a small amount of triplet reaction competing with energy transfer to nearest-neighbor diene molecules. The much more rapid rate of intersystem crossing in phenyl ketones relative to aliphatic ketones is the apparent cause for the lack of measurable singlet-state reaction in phenyl ketones. How the electronic configuration of the lowest triplet affects reactivity in type II processes will be dealt with later.

Biradical Intermediates in Triplet-State Reactions

The joint occurrence of both cyclization and elimination products involving 1,5-hydrogen transfer led Yang to suggest a 1,4 biradical as a common intermediate.[2] His suggestion was eminently reasonable not only because the observed products would be expected from such an intermediate but also because the known ease of intermolecular hydrogen atom abstraction by photoexcited ketones indicates that intramolecular hydrogen abstraction must be able to occur. We later opined



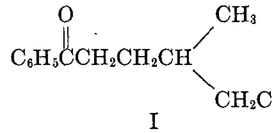
that the low quantum yields characteristic of type II reactions might well be due to disproportionation of the same biradical back to starting ketone,[10] as indicated by the reverse arrow in the equation. The observation of 1-methyl-3-cyclohexenol among the photoproducts of 6-hepten-2-one provided further evidence for a biradical intermediate.[12]

There is now little doubt that triplet ketones do in fact undergo type II processes exclusively *via* 1,4 biradicals. Prompted by an early report that ketones asymmetrically substituted at the γ position undergo some photoracemization,[13] we made a quantitative study of the behavior of (S)-(+)-4-methyl-1-phenyl-1-hexanone (I), the results of which are listed in Table I.[14]

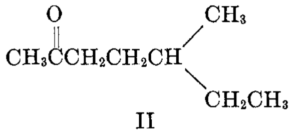
Table I
Quantum Yields for Photoreactions of (*S*)-(+)-4-Methyl-1-phenyl-1-hexanone[a]

Solvent	Φ_{II}[b]	Φ_{CB}[c]	Φ_{rac}[d]
Benzene	0.23	0.03	0.78 ± 0.05
Benzene + 2% *tert*-BuOH[e]	0.33	0.03	0.57 ± 0.05
tert-BuOH	0.94	0.06	0 ± 0.03[f]

[a] Degassed 0.10 M solutions irradiated at 3130 Å, 25°; $[\alpha]^{25}_{D}$ +9.8° (benzene). [b] Acetophenone formation. [c] Cyclobutanol formation. [d] Racemization of starting material, corrected to zero conversion. [e] 2% *tert*-butyl alcohol (by volume) in benzene. [f] At 16% conversion.



I



II

In benzene, the total quantum yield for product formation is only 0.26, while photoracemization is three times as efficient; the total quantum yield for observable photoreactions is thus within experimental error of unity. This experiment establishes two facts. First, 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 ground state of ketone. Second, this intermediate is formed in 100% efficiency from the triplet, in accord with our various suggestions based on solvent effects and kinetics that the triplet ketones undergo no direct physical decay.[10,15,16] Scheme I is strongly suggested, with $k_{\mathrm{rot}} > (k_{\mathrm{dis}} + k_{\mathrm{cy}} + k_{\mathrm{so}})$ and $k_{\mathrm{r}} \gg k_{\mathrm{d}}$.

The last two entries in Table I reaffirm our previous observations that polar solvents such as alcohols increase the quantum efficiency of triplet-state type II reactions.[15,17] A small amount of added alcohol produces an increase in product quantum yield which is compensated for by a decrease in racemization efficiency. In alcohol solvent, products are formed with 100% efficiency and there is no racemization observed. The explanation that hydrogen bonding by the hydroxy biradical to solvent molecules should effectively suppress disproportionation[15] seems to have gained general acceptance. The ability of the solvent to accept hydrogen bonds determines its effectiveness. Thus pyridine is even better than alcohols at enhancing type II quantum yields.[18]

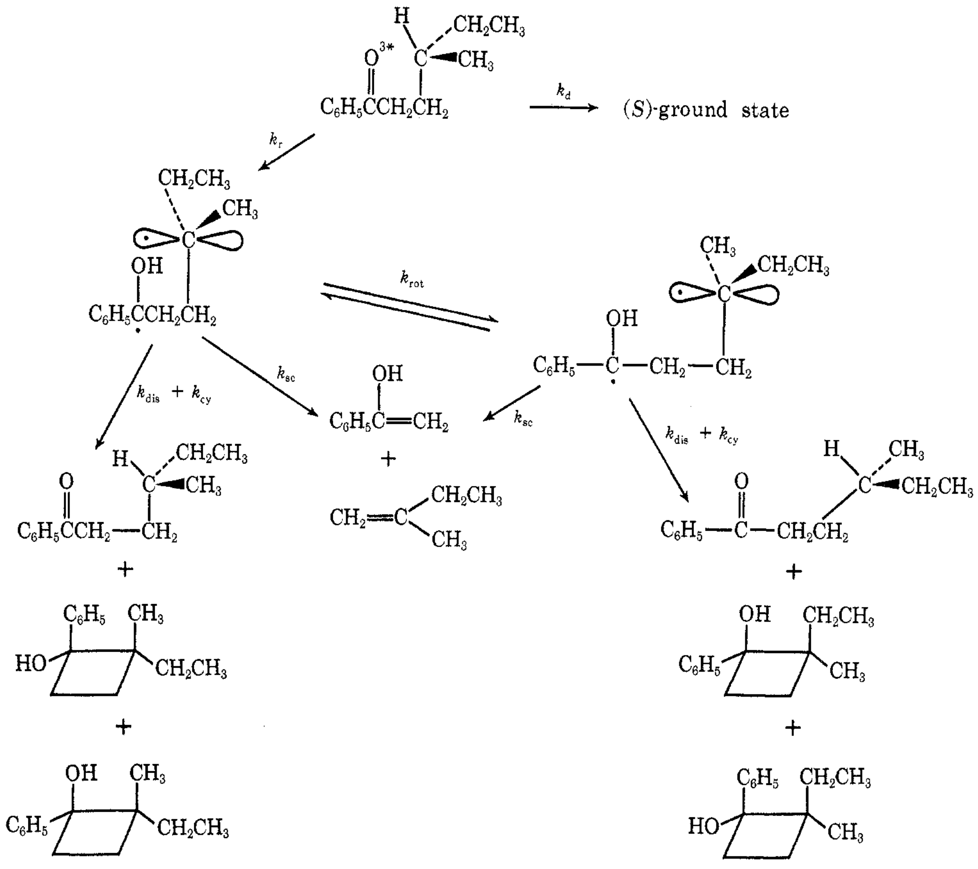
Yang has reported very similar results for the triplet-state type II processes of aliphatic ketones, as listed in Table II.[9] Note that all the triplets formed either give new products or racemize. Alcohol solvent decreases the amount of racemization but *does not eliminate it.* In general, polar solvents can suppress only about half the radiationless decay of triplet aliphatic ketones.[17]

There is evidence that triplet-state type II photoelimination proceeds *via* a biradical intermediate even when energetically it could proceed concertedly. Irradiation of III at 3650 Å yields stilbene which is 98–99% trans.[19] Consideration of bond energies indi-

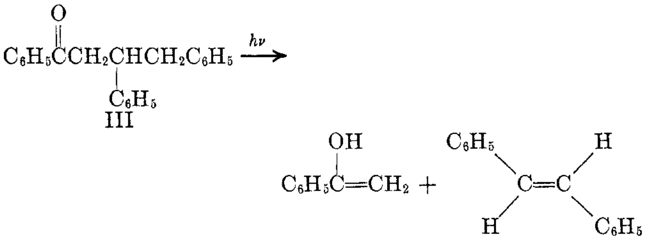
---

(10) P. J. Wagner and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 1245 (1966).
(11) P. J. Wagner and I. Kochevar, *ibid.*, **90**, 2232 (1968).
(12) N. C. Yang, A. Morduchowitz, and D. H. Yang, *ibid.*, **85**, 1017 (1963).
(13) K. H. Schulte-Elte and G. Ohloff, *Tetrahedron Lett.*, 1143 (1964).
(14) P. A. Kelso, unpublished results.
(15) P. J. Wagner, *J. Amer. Chem. Soc.*, **89**, 5898 (1967).
(16) P. J. Wagner and A. E. Kemppainen, *ibid.*, **90**, 5896 (1968).
(17) P. J. Wagner, *Tetrahedron Lett.*, 1753 (1967); 5385 (1968).
(18) A. E. Kemppainen, unpublished results.

Scheme I



cates that the conversion of triplet III into acetophenone enol and stilbene is at least 50 kcal exothermic, so that the system has enough energy for the concerted formation of triplet stilbene. Such must not happen, because triplet stilbene would have decayed to a 60:40 cis:trans mixture.[20]


$$C_6H_5\overset{O}{\overset{\|}{C}}CH_2\underset{\underset{C_6H_5}{|}}{C}HCH_2C_6H_5 \xrightarrow{h\nu} C_6H_5\overset{OH}{\overset{|}{C}}{=}CH_2 + C_6H_5CH{=}CHC_6H_5$$

III

Since there are two short-lived intermediates in triplet-state type II processes, structural variations produce two independent effects, one on excited-state reactivity and one on biradical reactivity. I have tried to keep the two topics as separate as possible in the following sections.

Triplet-State Kinetics

Scheme I portrays the various rate processes which enter into triplet-state type II reactions. Equation 1 defines, in terms of rate constants, the quantum yield for product formation, which is the only kinetic quantity measurable under steady-state irradiation conditions.

Table II
Quantum Yields for Photoreactions of (S)-(+)-5-Methyl-2-heptanone (II)

Solvent	Φ_{II}	Φ_{CB}	Φ_{RAC}	Φ_{isc}[a]	Φ^S[b]	Φ^T[b]
Hexane	0.13	0.025	0.08 ± 0.02	0.11 (0.18)	0.07	0.17
tert-BuOH	0.16	0.029	0.04 ± 0.02	0.11 (0.18)	0.07	0.16
2.5 *M* diene	0.065	0.005	0.002 ± 0.01	0.11 (0.18)	0.07	0

[a] Intersystem crossing yield in ref 7. Values in parentheses measured at Michigan State University. [b] Total quantum yields for observable reactions from singlet and triplet states. Slightly different values are suggested in ref 7.

$$\Phi_p = \Phi_{isc}\Phi_R P_p \tag{1}$$

$$\Phi_R = k_r\tau_T = \frac{k_r}{k_r + k_d} \tag{2}$$

$$P_p = (k_{sc} + k_{cy})\tau_{BR} = \frac{k_{sc} + k_{cy}}{k_{sc} + k_{cy} + k_{dis}} \tag{3}$$

For n,π* ketone triplets, $k_r \gg k_d$, so that $k_r = 1/\tau_T$, and $\Phi_p = \Phi_{isc}P_p$. In the case of phenyl ketones, $\Phi_{isc} = 1$ and $\Phi_p = P_p$. In both cases, quantum yields are determined by the behavior of the biradical intermediate and bear no relation to triplet-state reactivity.

Triplet lifetimes and thus k_r values are most conveniently measured by Stern–Volmer quenching studies

---

(19) P. J. Wagner and P. A. Kelso, *Tetrahedron Lett.*, 4151 (1969); R. A. Caldwell and P. Fink, *ibid.*, 2987 (1969).

(20) G. S. Hammond, *et al.*, *J. Amer. Chem. Soc.*, **86**, 3197 (1964).

under steady-state conditions. Intramolecular hydrogen abstraction is so rapid that 0.1–100-nsec triplet lifetimes result, too short to be measured by current flash techniques. Equation 4 is the familiar Stern–Volmer equation, plots of which—with which the literature now abounds—are linear, with slopes equal to $k_q\tau_T$, whenever only one excited state is reactive and quenched.

$$\Phi^0/\Phi = 1 + k_q\tau_T[Q] \qquad (4)$$

The rate constant k_q for exothermic energy transfer from ketone triplets to molecules such as naphthalene or conjugated dienes depends on solvent viscosity[11] (diffusion controlled) and is $5 \times 10^9\ M^{-1}\ \text{sec}^{-1}$ in benzene at 25°.[21]

Reactivity of Phenyl Ketone Triplets

Dependence on γ C–H Bond Strength. Table III contains quantum yields for type II photoelimination in benzene and k_r values for 12 phenyl ketones with different substituents on the γ carbon and therefore with different γ C–H bond strengths.[16,18] The quantum yields vary in benzene but approach unity in *tert*-butyl alcohol. The rate constants increase as the bond strength decreases, as expected for hydrogen atom abstraction. For example, the relative reactivities of tertiary:primary C–H bonds is 165:1. In the last eight compounds, the γ C–H bonds are all secondary, but the substituents all stabilize radicals more than does a mere methyl group. The benzylic and allylic C–H bonds are both more reactive than the simple C–H bonds in valerophenone. The electron-donating substituents hydroxy, methoxy, and dimethylamino all enhance reactivity, while the electron-withdrawing groups all decrease reactivity substantially. It would appear that the radical-stabilizing effects of the latter groups are offset by their inductive effects. It should be noted that the primary triplet state reaction of the dimethylamino-substituted ketone most likely is not hydrogen atom abstraction but rather charge transfer from nitrogen to the excited carbonyl.[22]

Inductive Effects on Reactivity. The inductive effects noted for γ substituents also appear for δ and ϵ substituents, as listed in Table IV.[18] In all these compounds, the γ C–H bond strength should be constant, such that pure inductive effects are involved. The strong dependence of k_r on σ_I constants indicates a Hammett ρ of -2 for the δ substituents. The triplet benzoyl group thus is a very electrophilic species, such that strong electron-withdrawing groups still exert measurable deactivation even when out in the ϵ position.

Steric Effects. As shown in Table III, γ-*tert*-butylbutyrophenone is slightly more reactive than valerophenone. Consequently, γ substituents produce no steric hindrance to hydrogen transfer. The length of the alkyl chain also produces no great alteration in the reactivity of the ketone triplet,[23] although ~5% δ-hydrogen abstraction may be occurring in hexanophenone and longer ketones.[14]

Table III
Effects of γ Substituents on Triplet-State Reactivity of $C_6H_5COCH_2CH_2CHR_1R_2$

R_1	R_2	Φ_{II}^a	$10^{-8}k_r$, sec^{-1}
H	H	0.36	0.08
CH_3	H	0.33	1.3
CH_3	CH_3	0.25	4.8
$C(CH_3)_3$	H	0.24	2.0
C_6H_5	H	0.50	4.2
$CH_2{=}CH$	H	0.26	5.0
OH	H	0.31	3.9
OCH_3	H	0.23	6.2
$N(CH_3)_2$	H	0.03	4.0
Cl	H	0.09	0.3
CO_2CH_3	H	0.50	0.1
CN	H	0.30	0.05

^{a} 0.10 M ketone in benzene, 3130 Å irradiation.

Table IV
Inductive Effects on Triplet-State Reactivity of $C_6H_5COCH_2CH_2CH_2CH_2R$

R	Φ_{II}	$10^{-8}k_r$, sec^{-1}	σ_I
H	0.33	1.3	0
Alkyl	0.30	1.5	−0.05
COC_6H_5	0.34	0.5	0.28
CO_2CH_3	0.63	0.4	0.30
Cl	0.58	0.2	0.47
CN	0.46	0.1	0.56
CH_2Cl	0.44	0.6	~0.20

More interesting effects are observed with phenyl cycloalkyl ketones, in which conformational factors can keep γ hydrogens away from the excited carbonyl. The phenyl cyclopentyl ketone triplet is only one-eighth as reactive as that of valerophenone.[24] The triplet state of *exo*-2-benzoylbicyclo[2.1.1]pentane, in which γ hydrogens are held near the carbonyl, is more reactive than that of valerophenone,[25] whereas the triplet lifetime of benzoylcyclobutane is very long.[26] Phenyl cyclohexyl ketone does not undergo any type II processes.[24]

Comparison with Alkoxy Radicals. It has been noted often that, in terms of simple valence bond pictures, the n,π* excited state of carbonyl compounds resembles an alkoxy radical.[27] Previous semiquantitative studies indeed indicated that in intermolecular hy-

radical ^{3}n,π* state

---

[21] W. D. K. Clark, A. D. Litt, and C. Steel, *J. Amer. Chem. Soc.*, **91**, 5413 (1969); G. Porter and M. R. Topp, *Proc. Roy. Soc., Ser. A*, **315**, 163 (1970).

[22] P. J. Wagner and A. E. Kemppainen, *J. Amer. Chem. Soc.*, **91**, 3085 (1969).

[23] J. N. Pitts, Jr., D. R. Burley, J. C. Mani, and A. D. Broadbent, *ibid.*, **90**, 5900 (1968).

[24] A. Padwa and D. Eastman, *ibid.*, **91**, 462 (1969).

[25] A. Padwa, *Accounts Chem. Res.*, **4**, 48 (1971).

[26] A. Pawda, E. Alexander, and M. Niemcyzk, *J. Amer. Chem. Soc.*, **91**, 456 (1969).

[27] P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, **5**, 21 (1968).

Table V
Relative Reactivities of C–H Bonds

C–H bond	Benzoyl[3]* (type II)	*tert*-BuO·[a]
CH_3	1	1
CH_2R	24	13
CHR_2	180	70
$CH_2C_6H_5$	80	45
CH_2–vinyl	90	60
CH_2OCH_3	116	60
CH_2Cl	5.5	5
CH_2CN	0.9	0.7
$\mathit{CH_2}CH_2COOH$	5.0	3.6[c]
$\mathit{CH_2}CH_2Cl$	4.0	4.5[b]
$\mathit{CH_2}CH_2CN$	1.3	1.4[b]
$\mathit{CH_2}CH_2CH_2Cl$	10	9[b]

[a] All from ref 29. [b] See also C. Walling and B. B. Jacknow, *J. Amer. Chem. Soc.*, **82,** 6113 (1960). [c] N. C. Deno, R. Fishbein, and J. C. Wyckoff, *ibid.*, **92,** 5274 (1970).

drogen abstraction triplet benzophenone displays a selectivity toward C–H bonds similar to that exhibited by the *tert*-butoxy radical.[28] Table V compares our intramolecular relative rate constants for the triplet benzoyl group to those found in Walling's laboratories for the *tert*-butoxy radical.[29] The parallel in selectivities, with regard to both C–H bond strength and inductive effects, is remarkable. The alkoxy radical is a very good model for the n,π^* ketone triplet, at least with regard to hydrogen abstraction. Relative reactivities of ketone triplets in α cleavage also resemble those displayed by *tert*-alkoxy radicals.[30] It remains to be seen how closely the hydrogen abstraction: α-cleavage ratios of ketone triplets resemble those of alkoxy radicals.

Aliphatic Ketone Triplets. Since the singlets of aliphatic ketones also undergo type II elimination, Stern–Volmer quenching plots of total reaction curve, and it is a little tricky extracting $k_q\tau_T$ values. Fortunately, these can be obtained in an alternate fashion in which the ketones are used to sensitize the triplet-state reaction of a quencher. Equation 5 describes the reciprocal dependence of sensitized quantum yield on quencher concentration (Φ_{isc} is the intersystem crossing yield of the donor ketone and α is the probability that

$$\Phi_{sens}^{-1} = \Phi_{isc(K)}^{-1}\alpha^{-1}\left(1 + \frac{1}{k_q\tau_T[Q]}\right) \tag{5}$$

the quencher triplet will yield the observed product. Figure 1 displays the dependence of the sensitized quantum for cis → trans isomerization of 1,3-pentadiene with 2-pentanone, 2-hexanone, and 5-methyl-2-hexanone as sensitizers. The kinetic parameters derived from these plots are listed in Table VI. Both the relative and absolute k_r values are very similar to those found for the analogous phenyl ketones (Table III). (Our original suggestion[10] that aliphatic triplets are much more reactive than aromatic triplets was, unfortunately, based on nonequivalent analytical methods.)

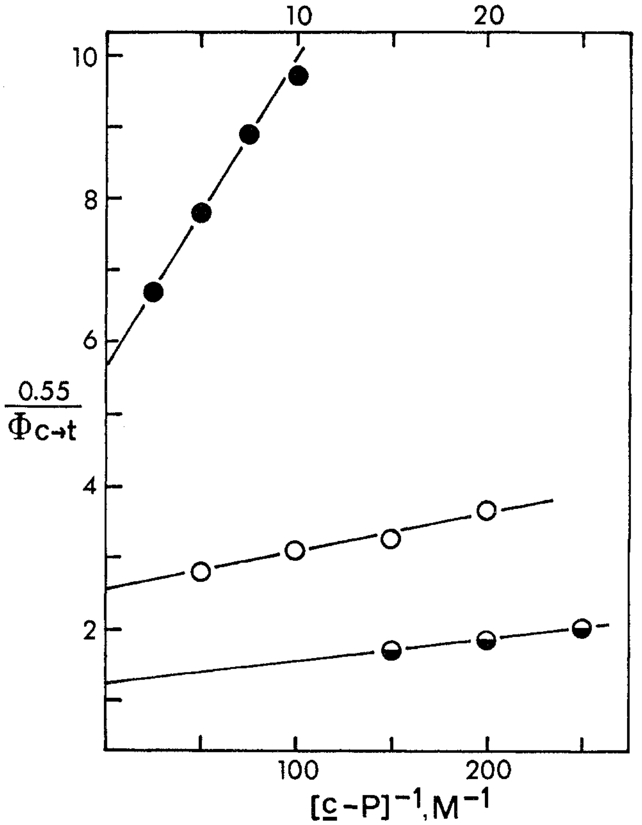


Figure 1. Dependence of quantum yields for sensitized cis → trans isomerization of 1,3-pentadiene on pentadiene concentration: ●, 5-methyl-2-hexanone, ○, 2-hexanone (both on upper abscissa scale): ◒, 2-pentanone (bottom scale); all ketones 0.15 *M* in benzene, 3130-Å irradiation.

Table VI
Triplet Lifetimes of Aliphatic Ketones $CH_3COCH_2CH_2CHR_1R_2$ as Determined by Sensitization of 1,3-Pentadiene Isomerization

R_1	R_2	Φ_{isc}[a]	$k_q\tau_T$[b]	$10^{-8}k_r$, sec^{-1}
H	H	0.81	390	0.13
CH_3	H	0.37	50	1.0
CH_3	CH_3	0.18	13	3.8

[a] Relative to Φ_{isc} = 1 for acetone. [b] In benzene.

Stereospecificity and Biradical Lifetimes

The biradicals obtained from different ketone triplet states differ quantitatively in their response to polar solvents.[31] Whereas type II quantum yields for phenyl ketones reach unity at 2–3 *M* *tert*-butyl alcohol, even in alcohol solvent aliphatic ketone triplets do not react 100% efficiently. One might infer that the phenyl biradicals are longer lived than the aliphatic biradicals.

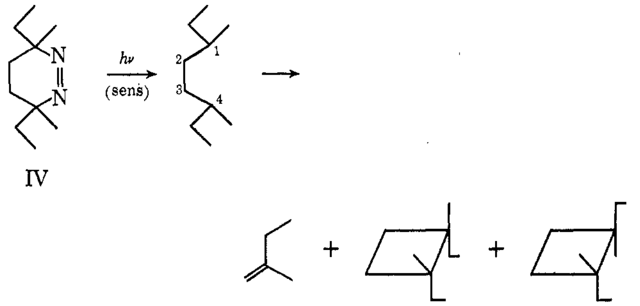
The actual lifetimes of even the longer-lived 1,4 biradicals which intervene in type II processes are not long enough to allow the biradical to be trapped by tributylstannane. We have looked for such trapping in vain.[32] Since alkyl radicals abstract hydrogen from the stannane with a rate constant of 10^6 M^{-1} sec^{-1}, we can place an upper limit of 10^{-7} sec on the lifetime of

---

(28) C. Walling and M. J. Gibian, *J. Amer. Chem. Soc.*, **87,** 3361 (1965); A. Padwa, *Tetrahedron Lett.*, 3465 (1964).
(29) C. Walling and M. J. Mintz, *J. Amer. Chem. Soc.*, **89,** 1515 (1967).
(30) P. J. Wagner and R. W. Spoerke, *ibid.*, **91,** 4437 (1969).
(31) I. Kochevar, unpublished results.
(32) R. G. Zepp, unpublished results.

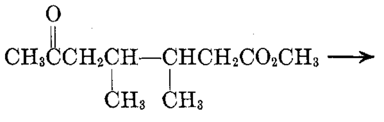
the valerophenone-derived biradical. The actual lifetime may be no more than 10^{-9} sec.

Biradical lifetimes are especially important when one considers the stereospecificity of their reactions. Apparently 1,4 biradicals do not live long enough to establish complete rotational equilibration. In the only published study of hydrocarbon 1,4 biradicals, Bartlett and Porter found that the biradical formed from *meso*- or *dl*-IV undergoes 4% inversion before cyclizing when formed as a singlet, 37% inversion when formed as a triplet.[33] Kinetic analysis of these results indicates that the singlet biradical reacts thirty times faster than the triplet biradical, with the latter reacting about half as fast as rotation about a 1,2 bond. Therefore, even though spin–spin interactions in a 1,4 biradical are expected to be small, the rate of spin inversion is still rate determining in the reactions of the triplet-generated biradical.



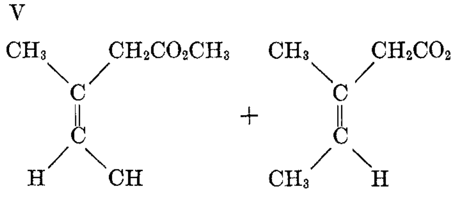
IV

Similar results exist for the triplet biradicals involved in type II processes. Stephenson has found that the two diastereomers of V react almost stereospecifically from their singlets and yield different cis:trans product ratios from their triplets.[34]



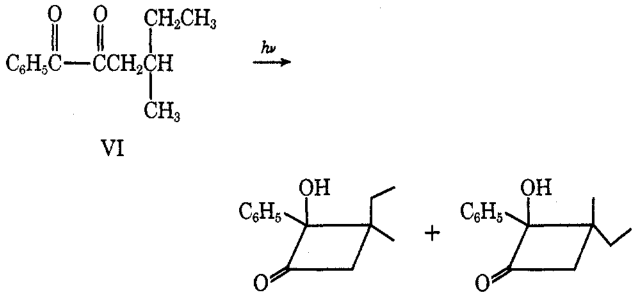
$$CH_3\overset{\overset{O}{\|}}{C}CH_2\underset{CH_3}{CH}—\underset{CH_3}{C}HCH_2CO_2CH_3 \longrightarrow$$

V



erythro (triplet)	→ 51%	49%
threo (triplet)	→ 35%	65%
erythro (singlet)	→ 98.9%	1.1%
threo (singlet)	→ 1.1%	98.9%

The presumably longer-lived biradicals from phenyl ketones such as I live long enough to *almost* equilibrate. However, the mixture of diastereomeric cyclobutanols formed from I does retain a small amount of optical activity.[14] We cannot judge the exact degree of retention of configuration,but we estimate it to be small and assume that the corresponding small percentage of retention in the re-formation of I is lost in experimental error. Likewise, the photocyclization of the optically active α-diketone VI results in a cyclobutanone mixture with a small optical rotation.[35]

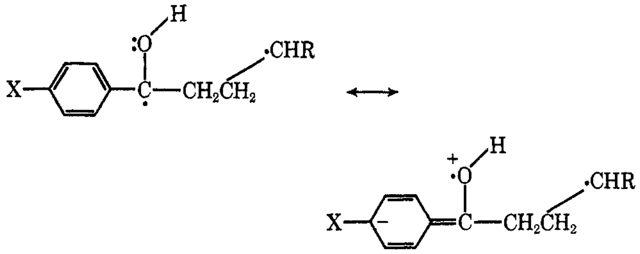


VI

It has been known for some time that the type II photocyclization of aliphatic ketones proceeds with some retention of configuration at the γ carbon.[13,36] A quantitative analysis is impossible, but my previous discussion should indicate that much of the retention may involve short-lived triplet biradicals as well as ultra-short-lived singlet biradicals.

Substituent Effects on "Triplet" Biradical Reactions

Inductive Effects. The effects of added alcohol on type II quantum yields of several ring-substituted valerophenones[37,38] indicate that electron-withdrawing groups decrease P_p and electron-donating groups enhance P_p. The present rationalization of this behavior is based on the fact that the hydrocarbon biradicals studied by Bartlett and Porter[33] undergo very little disproportionation. Since alkyl radicals are nucleophilic in their reactions, the large amount of disproportionation by type II biradicals must be due to the acidic nature of the O–H bond. Any substituent which enhances that acidity would lower P_p, and *vice versa*.



The larger-than-normal quantum yields for the ketones with electron-withdrawing groups at the γ and δ positions (Tables III and IV) may well reflect a reduced nucleophilicity of the γ-radical site in the biradical intermediates, while the lower-than-normal quantum yields for ketones with extra alkyl and methoxy groups at the γ or δ positions (Tables III and V) probably reflect the opposite effect.

Steric Effects. Although ring and γ substituents produce large changes in the percentage of disproportionation undergone by the biradicals, they do not affect the cyclization:elimination ratio very much.

---

[33] P. D. Bartlett and N. A. Porter, *J. Amer. Chem. Soc.*, **90**, 5317 (1968).

[34] L. M. Stephenson, P. R. Cavigli, and J. L. Parlett, submitted for publication.

[35] R. G. Zepp and P. J. Wagner, *ibid.*, **92**, 7466 (1970); N. J. Turro and T. J. Lee, *ibid.*, **92**, 7467 (1970).

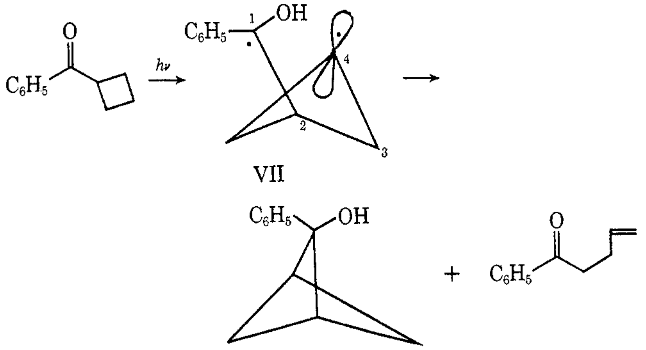
[36] I. Orban, K. Schaffner, and O. Jeger, *ibid.*, **85**, 3033 (1963).

[37] P. J. Wagner and H. N. Schott, *ibid.*, **91**, 5385 (1969).

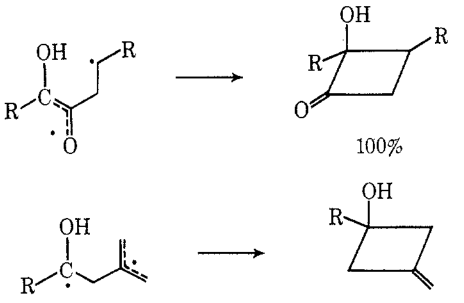
[38] P. J. Wagner and G. Capen, *Mol. Photochem.*, **1**, 173 (1969).

Steric factors introduced in cyclic systems and by α and β substituents do, however, produce marked effects.

We suggested some time ago that substituents could affect the ease with which the biradicals reach the necessary conformation for cleavage.[16] Since efficient cleavage requires maximum p-orbital overlap of the developing double bonds, the best conformation must be one in which the p orbitals at carbons 1 and 4 are both parallel to the 2,3 carbon–carbon bond. We cited as the best evidence then available the remarkable behavior of phenyl cyclobutyl ketone, which upon irradiation undergoes 60% cyclization to the highly strained bicyclopentane system and only 40% cleavage to the strain-free acyclic system.[26] Surely product stabilities do not dominate the competition. In the biradical VII, the p orbital at C-4 is held almost perpendicular to the 2,3 C–C bond such that the phenylpentenone product must develop with a twisted terminal double bond. This reasoning probably explains the behavior of several cyclic ketone systems.[39]


VII

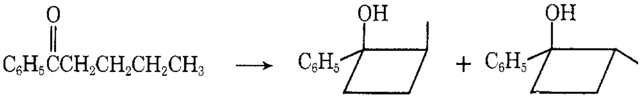
It has been known for some time that α diketones[40] and β,γ-unsaturated ketones[41] with γ C–H bonds undergo only cyclization and no type II elimination. In each case, one radical site in the biradical intermediate is allylic such that its π system is completely orthogonal to the 2,3 C–C bond. This conformational effect is probably the major cause of the lack of elimination. The necessity for breaking bonds to sp²-hybridized carbons may contribute further to lowering the rate of cleavage of such biradicals.



Both we[42] and Lewis[43] find that α and β substituents greatly alter the cyclization:elimination ratios of acyclic ketones. Thus, α,α-dimethylvalerophenone undergoes >80% cyclization *vs.* 15% for unsubstituted valerophenone. In contrast, β,β-dimethylbutyrophenone undergoes little, if any, cyclization.

There is not space here to go into a detailed rationalization of these effects, nor is enough information now available for the formulation of a satisfactory general explanation. One dominant principle can be stated. With their short lifetimes, the biradicals can undergo only a few rotations before reacting. Consequently, if a substituent introduces a substantial barrier to some rotation which is necessary to bring the biradical into a conformation required for reaction, that rotation may become rate determining. Examination of models reveals considerable 1,2-eclipsing interactions in the most likely conformation for cleavage, which may explain the retarding effects of α substitution. Likewise, development of 1,3-diaxial interactions during cyclization may explain the retarding effects of β substitution.

The stereoselectivity noted in the photocyclization of valerophenone[15] attests to the importance of developing steric interactions in 1,4-biradical closures. In hexane, the trans:cis ratio of the cyclobutanol products is 5:1. Interestingly, the ratio drops to 2:1 in *tert*-butyl alcohol and the total yield of cyclization decreases somewhat. The solvated hydroxyl group must approach phenyl in steric bulk, such that most of the stereoselectivity is lost.



Effects of Substituents on Triplet-State Reactivity of Benzoyl Group

α Substituents. Electronegative groups at the α carbon enhance the photoreactivity of carbonyl triplets. For example, the results of Evans and Leermakers indicate that triplet α-ketodecanoic acid is 3–5 times more reactive than triplet 2-hexanone.[44] The triplet-state reactivity of α-ethoxyacetophenone[45] is 14 times greater than that of γ-methoxybutyrophenone (Table III). In both ketones the γ carbon is secondary and bonded to an ether oxygen, so that the γ C–H bond strengths should be identical. Likewise, triplet α-methoxyacetophenone is some 200 times more reactive than triplet butyrophenone.[16,45] The enhanced reactivity of the α-alkoxyketones apparently reflects an inductive effect on the triplet benzoyl. Thus triplet α-methoxybutyrophenone abstracts a γ hydrogen from its propyl group six times more rapidly than does triplet butyrophenone itself.[45] Lewis and Turro have suggested that the presence of an oxygen atom in the

---

(39) R. B. Gagosian, J. C. Dalton, N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 4752 (1970).

(40) W. H. Urry and D. J. Trecker, *ibid.*, **84**, 118 (1962).

(41) N. C. Yang and D. M. Thap, *Tetrahedron Lett.*, 3671 (1966).

(42) A. E. Kemppainen and J. McGrath, unpublished results.

(43) F. D. Lewis and T. A. Hilliard, *J. Amer. Chem. Soc.*, **92**, 6672 (1970).

(44) T. R. Evans and P. A. Leermakers, *ibid.*, **90**, 1840 (1968).

(45) N. J. Turro and F. D. Lewis, *ibid.*, **92**, 311 (1970).

Table VII

Effects of Ring Substituents on Type II Photoelimination of Phenyl *n*-Butyl Ketones

Substituent	$\Phi_{\max}{}^{a}$	$1/\tau$, 10^7 sec^{-1}	k_r, 10^7 sec^{-1}
p-CH_3O	0.26	0.22	0.06
p-CH_3	1.00	2.0	1.6
p-Cl	0.80	3.7	3.0
H	1.00	14.0	14.0
o-CF_3	1.00	13.0	13.0
m-(N)^{b}	1.00	31.0	31.0
p-CF_3	1.00	29.0	29.0

[a] Maximum quantum yield for reaction of ketone upon addition of alcohol. [b] 3-Pyridyl ketone.

six-membered transition state for γ-hydrogen abstraction also enhances the rate.[45]

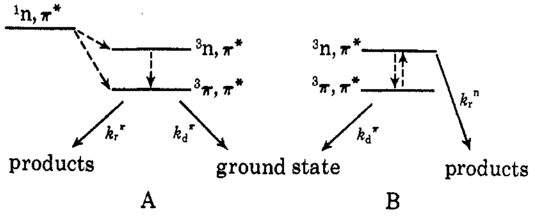
Ring Substituents. Both electron-donating and electron-withdrawing substituents lower type II quantum yields, but for different reasons: the latter affect the biradical, the former affect the triplet state. Table VII contains data for some representative compounds.

Inductive Effects on n,π Triplets.* Unsubstituted phenyl ketones and those with electron-withdrawing substituents all have phosphorescence lifetimes shorter than 10 msec at 77°K and thus have n,π* lowest triplets. They all undergo type II processes in 100% efficiency in alcohol solvent and thus undergo no direct decay from their triplet states. The strong electron-withdrawing groups double triplet-state reactivity, which effect seems best interpreted as a simple inductive effect on the electrophilic species.[38] Similarly, Yang has found that methyl groups slightly decrease the reactivity of the n,π* triplet of benzophenone.[46] These inductive effects are noteworthy primarily for their smallness.

Inversion of Triplet States. It is now well known that the π,π* triplets of unsubstituted phenyl alkyl ketones lie only a few kilocalories above the n,π* triplets.[47] Electron-donating substituents of any kind as well as high solvent polarity invert the order of states. Thus the chloro-, methyl-, and methoxy-substituted ketones have phosphorescence lifetimes greater than 50 msec at 77°K. Small amounts of added alcohol produce maximum type II quantum yields lower than unity, while large amounts *decrease* quantum yields. Obviously, some direct triplet decay competes with γ-hydrogen abstraction. All these ketones with π,π* lowest triplets show substantially reduced reactivity in intramolecular hydrogen abstraction.[48] The same phenomenon has been observed for intermolecular reactions of substituted acetophenones.[49]

The resistance of naphthyl and of p-amino ketones toward photoreduction is notorious. The classical explanation is that such ketones have π,π* triplets lying far below their lowest n,π* triplets.[50] Unlike the n,π* triplets, the π,π* states have most of their excitation localized in the aromatic rings and, in particular, have an electron-rich rather than an electron-deficient carbonyl oxygen, so that their lack of radical-like reactivity is not surprising. In Table VII, however, we have a group of ketones whose n,π* triplets lie only a few kilocalories above their lowest π,π* triplets and which undergo photoinduced hydrogen abstraction quite efficiently. The question which must be answered, a question not unique to type II reactions, is by what mechanism the proximity of a n,π* triplet imparts photoreactivity to ketones with π,π* lowest triplets. Scheme II illustrates two extreme possibilities.

Scheme II



Scheme IIA assumes that only the lowest triplet reacts. Since spectroscopists tell us that n,π* and π,π* triplets mix vibronically, Yang has suggested that the small amount of n,π* character mixed into the lowest triplets gives those states some n,π*-like reactivity.[49] Scheme IIB assumes that π,π* triplets just are not reactive and that if the two triplets are within a few kcal of each other they can readily reach thermal equilibrium before decaying. In that case the photoreactivity of these ketones would arise from low equilibrium concentrations of the upper n,π* triplets.

If one were to adopt an either/or attitude, each extreme would be beset by troublesome facts. For example, could the lowest triplets of the p-chloro and p-methyl ketones be 21 and 11% n,π* in character, respectively? That is rather more mixing than is usually attributed to vibronic interactions. On the other hand, ascribing the known (albeit greatly reduced) triplet-state reactivity of naphthyl ketones[51] solely to equilibrium population of the n,π* triplet seems risky, given the 10 kcal or greater separation between it and the lowest π,π* state.

A balanced view assumes that either or both mechanisms may be operative in a given ketone. Equation 6 describes the equilibrium triplet-state lifetime and observed rate constants for the case of both states reacting. X_n and X_π are the fractions of triplets in the n,π* and π,π* states, respectively, at equilibrium.

$$1/\tau = k_r{}^{\text{obsd}} + X_\pi k_d{}^{\pi} = X_n k_r{}^{n} + X_\pi k_r{}^{\pi} + X_\pi k_d{}^{\pi} \quad (6)$$

X_n decreases exponentially with increasing separation of the states while vibronic mixing (and thus pre-

---

(46) N. C. Yang and R. L. Dusenbery, *Mol. Photochem.*, **1**, 159 (1969).

(47) A. A. Lamola, *J. Chem. Phys.*, **47**, 4810 (1967).

(48) P. J. Wagner and A. E. Kemppainen, *J. Amer. Chem. Soc.*, **90**, 5898 (1968).

(49) N. C. Yang and R. L. Dusenbery, *ibid.*, **90**, 5899 (1968).

(50) J. N. Pitts, Jr., H. W. Johnson, Jr., and T. Kuwana, *J. Phys. Chem.*, **66**, 2456 (1962).

(51) G. S. Hammond and P. A. Leermakers, *J. Amer. Chem. Soc.*, **84**, 207 (1962); A. G. Schultz, C. D. Deboer, W. G. Herkstroeter, and R. H. Schlessinger, *ibid.*, **92**, 6086 (1970).

Table VIII

Triplet-State Reactivity of *p*-Anisyl Ketones (p-$CH_3OC_6H_4CO(CH_2)_3R$)

R	Φ_{max}	$1/\tau$, 10^6 sec^{-1}	k_r^{obsd}, 10^6 sec^{-1}	k_d, 10^6 sec^{-1}
CH_3[a]	0.26	2.2	0.56	1.6
CH_2CN[a]	0.015	2.0	0.03	1.7
CH_3[b]	0.09	1.15	0.10	1.1

[a] In benzene. [b] In methanol.

Table IX

Reactivity of Singlet Aliphatic Ketones, $CH_3COCH_2CH_2CHR_1R_2$

R_1	R_2	$1/\tau_s$, 10^8 sec^{-1}	Φ_{isc}	k_r^s, 10^8 sec^{-1}	Φ_{II}^s
H	H	5.0	0.63	1.8	0.025
CH_3	H	14.0	0.27	8.6	0.10
CH_3	CH_3	24.0	0.13	21.4	0.10

sumably k_r^π) has a simple inverse dependence on the energy separation. Thus we might expect equilibration of states to be most important when the two states are very close together and vibronic mixing to take over when the two states are far apart.

In agreement with the above reasoning, we find that the observed k_r values for *p*-methoxyphenyl ketones have exactly the same dependence on γ C–H bond strength and are subject to the same inductive effects of γ and δ substituents as k_r^n for simple phenyl ketones.[52] As shown in Table VIII, k_r^{obsd} for the *p*-methoxy ketones in benzene averages 0.5% as large as for the phenyl ketones (Tables III and IV). We interpret this reactivity as coming from a n,π* triplet 3 kcal above the π,π* triplet. In methanol, k_r^{obsd} for *p*-methoxyvalerophenone is only 0.08% as large as for valerophenone, which further decrease we attribute to a 4-kcal separation of the two triplets. If the π,π* state of the anisyl ketones were reacting at a rate roughly $^1/_{200}$ of k_r^n, we would have expected it to be both more selective toward C–H bond strength and less subject to inductive effects.

We are currently studying ketones with larger n,π*–π,π* separations as well as temperature effects on photoreactivities to test the generality of the scheme I have presented here.

Reactivities of Aliphatic Ketone Singlets

As Table VI shows, quantum yields of intersystem crossing decrease markedly as the γ C–H bond strength decreases. This decrease in triplet formation is accompanied by increased singlet-state (unquenchable) type II elimination. Yang has measured singlet-state lifetimes by the ingenious technique of quenching the reaction with biacetyl (which quenches ketone singlets as well as triplets) in the presence of sufficient diene to quench almost all triplet reaction.[8] The slopes of the resultant Stern–Volmer plots yield $k_q\tau_s$ values. His data are reproduced in Table IX. As with triplet states, singlet-state lifetimes decrease as γ C–H bond strength decreases. Unlike triplet states, however, singlet-state quantum yields increase with increasing reactivity of the γ C–H bond.

Since $\Phi_{isc} + \Phi_{II}^s$ do not add up to anywhere near unity, substantial amounts of radiationless decay must take place from the singlet. There are two kinetic extremes for analyzing the results. One could assume that all decay comes directly from the excited state, calculate k_{isc} and k_r^s values from the appropriate quantum yields and τ_s, and then assume that $k_d^s = 1/\tau_s - (k_{isc} + k_r^s)$. If this reasoning is applied to the data in Table IX, one finds that k_d^s values increase as γ C–H bond strength decreases. Such a result indicates one of two things: (1) a γ C–H bond is involved in a direct physical decay process of the singlet, or (2) as with the triplet, $k_r^s > k_d^s$ and all the singlet reacts to yield some metastable intermediate which can go on to stable products or revert to ground-state reactant. I have assumed the latter in calculating the k_r^s values in Table IX, which are 5–10 times larger than the corresponding triplet k_r values.

Mechanism of Singlet-State Reaction

Singlet-state type II reactions differ in many other respects from the triplet reaction: (1) as mentioned earlier, the cyclization:elimination ratio is smaller; (2) the ratio radiationless decay:reaction is 11:1 for the singlet *vs.* 1:1 for the triplet;[9] (3) there is no polar solvent effect on singlet-state quantum yields;[9,17] (4) tributylstannane photoreduces most of the triplet but none of the singlet;[17] (5) as shown in Table II, decay of excited singlet II back to ground state occurs with little racemization at the γ carbon. Similarly, the excited singlets of V undergo elimination with high stereospecificity.[34]

Triplet alkanones quite clearly undergo intromolecular hydrogen abstraction to yield biradicals which are long-lived enough to racemize and to be solvated. It has been postulated that the singlet states also undergo simple intramolecular hydrogen abstraction to yield biradicals which are so short-lived that they undergo *no* solvation and negligible rotation about the β,γ carbon–carbon bond.[9] Although one surely cannot rule out the presence of singlet biradicals, there is some evidence that the overall singlet-state process is more complicated than the triplet-state process.

Electronic–Vibrational Energy Transfer

Hammond has pointed out that the chemical reactions of excited states are special forms of radiationless decay.[53] Heller has independently applied this concept to hydrogen atom abstractions by suggesting that transfer of electronic energy into vibrational modes of C–H bonds occurs as a discrete step preceding radical formation.[54] Quantum yields of product formation then depend on how the vibrationally hot *ground-state*

---

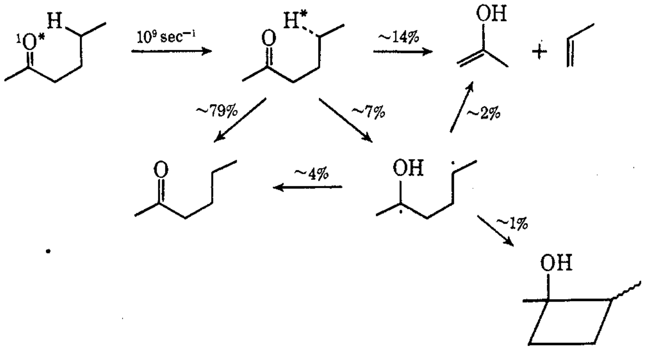
(52) P. J. Wagner, A. E. Kemppainen, and H. N. Schott, *J. Amer. Chem. Soc.*, **92**, 5280 (1970).

(53) G. S. Hammond, *Advan. Photochem.*, **7**, 373 (1969).

(54) A. Heller, *Mol. Photochem.*, **1**, 257 (1969).

species partitions its energy. Excited-state rate constants should depend on the stretching frequency of the bond being broken. It is worthwhile exploring whether this idea can explain singlet-state type II processes.

Scheme III



Scheme III estimates how excited singlet 2-hexanone might dissipate its excitation energy *via* interaction with a γ C–H bond. The relative percentages are based on the assumption that any singlet biradical partitions itself among products in the same way as does the biradical formed from triplet 2-hexanone. Unfortunately, there is kinetic evidence both for and against such electronic–vibrational energy transfer. If both singlet and triplet ketones abstracted hydrogen atoms by the same mechanism, the 10-fold greater reactivity of singlets toward γ C–H bonds (compare Tables VI and IX) is difficult to explain in comparison with the well-documented 100-fold greater reactivity of triplets toward Sn–H bonds.[55] However, the comparison makes sense in terms of radiationless decay theory. Since the Sn–H stretching frequency is only half as large as that for C–H, transfer of electronic energy into Sn–H stretching modes would be expected to be very much slower than into C–H stretches. On the other hand, radiationless decay theory would predict huge deuterium isotope effects. Experiments indicate that γ deuteration increases singlet ketone lifetimes by a factor of only three[7] or four.[56] Hopefully, further work will soon resolve this intriguing dilemma.

Acknowledgments are due to my diligent coworkers; to the National Science Foundation; to Professors Stephenson, Lewis, Padwa, and Turro for their generous sharing of unpublished results; and to N. C. Yang for first attracting my interest to type II reactions, and for regularly reinforcing that interest.

---

[55] P. J. Wagner, *J. Amer. Chem. Soc.*, **89**, 2503 (1967).
[56] A. Padwa and W. Bergmark, *Tetrahedron Lett.*, 5795 (1968).

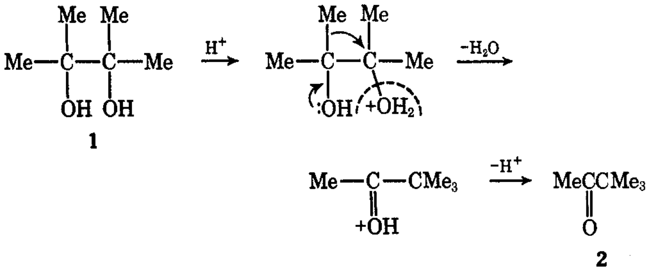
Migrations of Alkoxycarbonyl Groups

R. MORRIN ACHESON

Department of Biochemistry, Oxford, OX1 3QU, England

Received September 14, 1970

The subject of intramolecular rearrangement has fascinated chemists since the time of Fittig, who in 1860 discovered that pinacol (**1**) with sulfuric acid isomerized to pinacolone (**2**). Very many examples and types of rearrangements are now known; the tendency to form a more stable arrangement of atoms than that present in the starting material is the driving force for the reactions. This can be associated with the relief of steric strain, or the formation of aromatic or more conjugated systems, during the rearrangement.



Fittig's reaction proceeds by protonation of one hydroxyl group after which a methyl group migrates as water is eliminated. A very large number of rearrangements of this general type have been discovered, and both alkyl and aryl groups can move.[1] Relative

---

[1] G. W. Wheland, "Advanced Organic Chemistry," 3rd ed, Wiley, New York, N. Y., 1960, p 536 ff; P. de Mayo, Ed., "Molecular Rearrangements," Parts 1 and 2, Interscience, New York, N. Y., 1960.