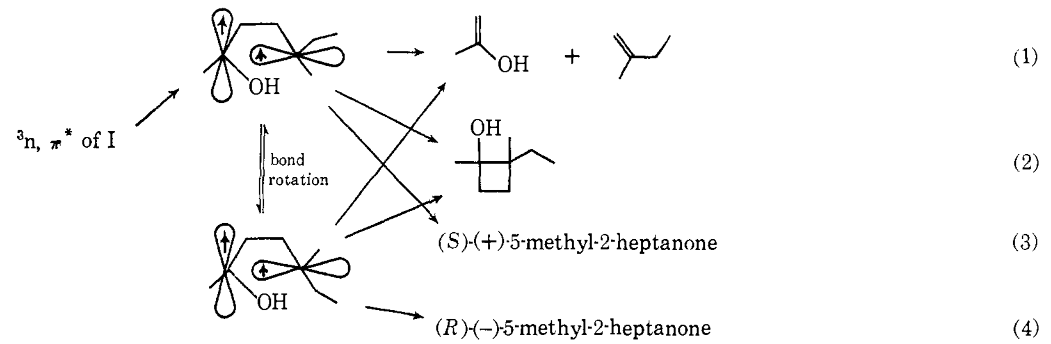

diate.[1] One may visualize that the ^{3}n,π^* state of I will give a triplet biradical (II). Spin inversion and fragmentation of II will give acetone and 2-methyl-1-butene (reaction 1), spin inversion and ring closure will give diastereomeric forms of 1,2-dimethyl-2-ethylcyclobutanol (reaction 2), and spin inversion and hydrogen transfer back to the C_5 position will give I (reaction 3). However, if the rotation around the C_4–C_5 bond occurs prior to the spin inversion and hydrogen transfer or ring closure, II will give racemic I or cyclobutanols (reaction 4). It is well known that the addition of triplet methylene to olefins is nonstereospecific; therefore, the rate of bond rotation in a triplet biradical is at least comparable to that of spin inversion alone.

We also found that I was slowly consumed upon irradiation even in the presence of high concentrations of 1,3-pentadiene, a behavior which differs from that of 2-hexanone.[4] Therefore, the true values of the triplet quantum yields are not reflected at high quencher concentrations. By extrapolating the Stern–Volmer plot to zero quencher concentration as in Figure 1, the quantum yield of type II process from the triplet state may be calculated to be 0.044 ± 0.006 in hexane. Similar treatment of the plot for the quantum yield of cyclobutanol formation gives a value of 0.017 ± 0.006 from the triplet state. Assuming the rate of rotation around the C_4–C_5 bond in II is much greater than the sum of the rate of spin inversion and the rate for hydrogen transfer back to the C_5 position (reaction 4), biradical II will give equal amounts of I and its enantiomer. Therefore, the sum of the quantum yields of observed events from the triplet state is 0.14 ± 0.02. By applying the technique of Hammond and Lamola,[5] we have estimated the intersystem crossing efficiency of I to be 0.11 ± 0.01, which is markedly low for carbonyl compounds. However, the value for intersystem crossing and the sum of all quantum yields from the triplet state are within experimental error of each other, as in the case of aromatic ketones. This observation suggests that the rate of bond rotation is indeed much faster than the combined rates of spin inversion and hydrogen transfer reaction; otherwise, the sum of all quantum yields from the triplet state would have been smaller than that for intersystem crossing. Since I does not fluoresce with appreciable efficiency, the difference between unity and the sum of all observed events, 0.78 ± 0.05, must be attributed to the efficiency of nonradiative decay from the singlet state.

In conclusion, we wish to report that the ^{3}n,π^* state of 5-methyl-2-heptanone (I) decays *via* a triplet biradical intermediate (II) while its ^{1}n,π^* state decays *via* a different route,[6] and that in contrast to analogous aromatic ketones the predominant nonradiative decay process of I takes place from the ^{1}n,π^* state.

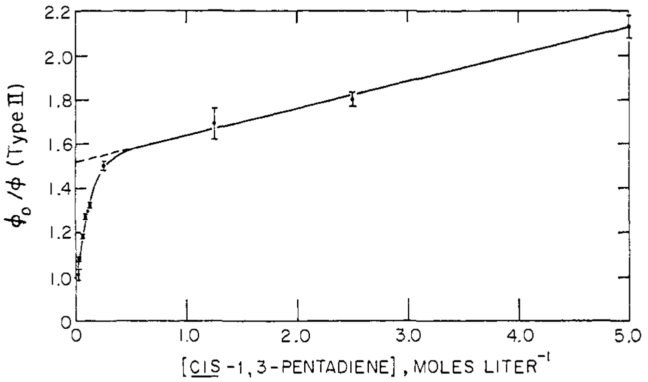

Figure 1.

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

[6] N. C. Yang, S. P. Elliott, and B. Kim, *J. Amer. Chem. Soc.*, **91**, 7551 (1969).

[7] The authors wish to acknowledge the National Science Foundation for the support of this work, the National Institutes of Health for a grant to purchase the spectropolarimeter used in this investigation, and Mrs. Antoinette Spears for her capable assistance in developing the synthesis of (*S*)-(+)-5-methyl-2-heptanone.

[8] National Science Foundation Trainee, 1966–1968; National Institutes of Health Predoctoral Fellow, 1968–1970.

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Received October 3, 1969

The Mechanism of Photochemistry of Alkanones with γ Hydrogens

Sir:

Photoexcited alkanones with γ hydrogens react almost exclusively *via* the type II process and cyclobutanol formation.[1] In contrast to aryl alkyl ketones with γ hydrogens, the quantum yields of photolyses of these alkanones in *t*-butyl alcohol fall short of unity.[2] Since the triplet state of these alkanones in *t*-butyl alcohol decays entirely *via* a biradical intermediate,[1,2] the principal nonradiative process must have occurred from their singlet excited state.[2] Generally a molecule in its lowest singlet excited state may undergo chemical reactions, intersystem crossing to a triplet state, fluorescence, and nonradiative decay back to the ground state with respective rates of k_s, k_{st}, k_f, and k_{-s} and quantum efficiences of ϕ_s, ϕ_{st}, ϕ_f, and ϕ_{-s}. In order to achieve a detailed analysis of the behavior of photoexcited alkanones with γ hydrogens, we examined the rates and efficiencies of various photochemical and photophysical processes of 2-pentanone (Ia), 2-hexanone (Ib), and 5-methyl-2-hexanone (Ic).

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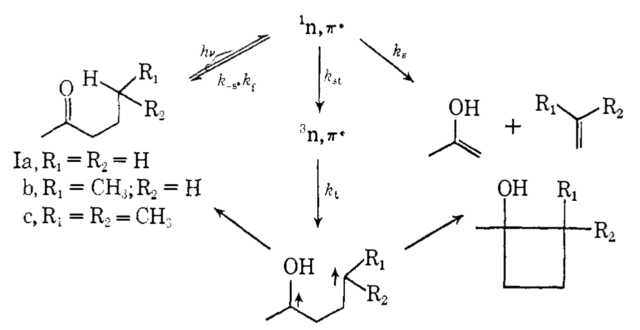
[1] For a review of these reactions see P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, **5**, 21 (1968).

[2] N. C. Yang and S. P. Elliott, *J. Amer. Chem. Soc.*, **91**, 7550 (1969).



II

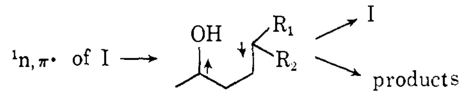
All irradiations were carried out in 1 *M* solution of the ketone in hexane. The quantum yield determinations were carried out with the aid of ferrioxalate actinometry[3] and checked with the benzophenone-*cis*-1,3-pentadiene[4] and 2-hexanone secondary actinometers. The yields for type II processes and cyclobutanol formations were followed quantitatively by vpc. The lifetimes of the singlet states of these ketones were determined from the slopes of Stern–Volmer plots ($k_q\tau_s$) using biacetyl as the energy acceptor in the presence of 0.5 *M* *cis*-1,3-pentadiene. Under such conditions, the reactions from the ^{3}n,π* state were virtually all quenched, and the remaining reactions may be taken as entirely due to the ^{1}n,π* state.[5] The efficiencies of intersystem crossing (ϕ_{st}) of these ketones were determined by the classical method developed by Lamola and Hammond using the triplet-sensitized isomerization of 1,3-pentadiene.[4] Since these ketones do not fluoresce or phosphoresce with appreciable efficiency at room temperature, the difference between unity and the sum of ϕ_s and ϕ_{st} may be taken as the efficiency of nonradiative decay from the singlet state (ϕ_{-s}). The lifetime of the singlet state is the reciprocal of the sum of all decay rates, *i.e.*, $1/\tau_s = k_s + k_{-s} + k_{st}$; therefore, we may calculate the rates for individual processes from the lifetime of the singlet state and the respective quantum efficiencies. The results are summarized in Table I.

Table I

	2-Pentanone (Ia)	2-Hexanone (Ib)	5-Methyl-2-hexanone (Ic)
$k_q\tau_s$, l. mol^{-1}	20.2	7.3	4.1
τ_s, sec[a]	2.02×10^{-9}	7.3 ± 10^{-10}	4.1×10^{-10}
ϕ_{st}	0.63 ± 0.04[b]	0.27 ± 0.02[b,c]	0.11 ± 0.01[b]
k_{st}, sec^{-1}	3.1×10^8	3.7×10^8	2.7×10^8
ϕ_s[d]	0.025	0.10	0.10
k_s, sec^{-1}	1.2×10^7	1.4×10^8	2.4×10^8
ϕ_{-s}	0.35 ± 0.04	0.63 ± 0.02	0.79 ± 0.02
k_{-s}, sec^{-1}	1.7×10^8	8.5×10^8	1.9 ± 10^9
ϕ_t[d]	0.36[e]	0.23	0.09

[a] k_q is assumed to be 1×10^{10} l. mol^{-1} sec^{-1}. [b] Small and variable amounts of pentadiene dimers were detected; in the case of Ic a small amount of an adduct of Ic and pentadiene was also formed. [c] ϕ_{st} of 2-hexanone is independent of 2-hexanone concentration ranging from 0.006 to 1.0 *M*. [d] The values include both type II process and cyclobutanol formation. [e] Substantial intermolecular reduction of 2-pentanone by the solvent was also detected, and a number of products including 2-pentanol have been tentatively identified. These products were formed from the triplet state of 2-pentanone as they were not formed in the presence of 0.5 *M* *cis*-1,3-pentadiene.

The results clearly indicate that the efficiency of the intersystem crossing (ϕ_{st}) decreases successively from 2-pentanone to 2-hexanone to 5-methyl-2-hexanone, while the rates of intersystem crossing (k_{st}) for these compounds remain essentially the same ($3.2 \pm 0.5 \times 10^8$ sec^{-1}). The decrease in ϕ_{st} in this series is due to the increase in both the rate for chemical reactivity from the singlet state (k_s) and the rate for nonradiative decay from the singlet state (k_{-s}). There is also a gradual decrease in the singlet-state lifetime (τ_s) in the series.[6] The principal difference among these compounds is the nature of the γ hydrogen, which varies from primary to secondary to tertiary. Therefore, both k_s and k_{-s} depend at least in part on the strength of the γ-C–H bond. As the bond energy decreases from primary to secondary to tertiary, the rate increases. Since k_{st}, the rate of a physical process from the singlet state, does not vary appreciably in this series, the results strongly imply that a chemical process may be involved in the k_{-s} of these alkanones. The simplest way to explain such a process in k_{-s} is the abstraction of γ hydrogen by the excited carbonyl group to form a singlet 1,4 biradical (III) as the primary step. III may undergo a reverse reaction to give the starting alkanone (I) to account for at least a substantial part of k_{-s}, or it may undergo fragmentation or cyclization to give products. III differs from the triplet biradical generated from the ^{3}n,π* state (II) in that it may undergo chemical transformations without spin inversion; therefore, it is not surprising that III and II may exhibit different chemical behavior.[2]



III

The concept is further demonstrated by an independent experiment. Irradiations of 6-hepten-2-one both in the absence and in the presence of 1,3-pentadiene yield a mixture of acetone, butadiene, *cis*-1-methyl-2-vinylcyclobutanol, *cis*-5-hepten-2-one,[7] and 1-methyl-3-cyclohexenol.[8] The formation of 1-methyl-3-cyclohexenol in the presence of 1,3-pentadiene, *i.e.*, from the singlet state, may be readily accounted for by a biradical intermediate. The formation of cyclohexenol in a completely concerted process would require a highly strained transition state with the C₅–C₆ bond twisted at such an angle that little delocalization can occur to the incipient C₅–C₆ double bond.

This concept may be applied to account for the results of two interesting observations in the literature. (1) The quantum efficiency of photolysis of *n*-butyl *t*-butyl ketone in solution is relatively low as compared to other *t*-butyl ketones.[9] The low efficiency may be now accounted for by the increase in k_{-s} which causes the decreases in ϕ_{st} and ϕ_t. (2) The quantum efficiency of

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[3] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.* (London), **A235**, 518 (1956); C. A. Parker, *ibid.*, **A220**, 104 (1953).

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

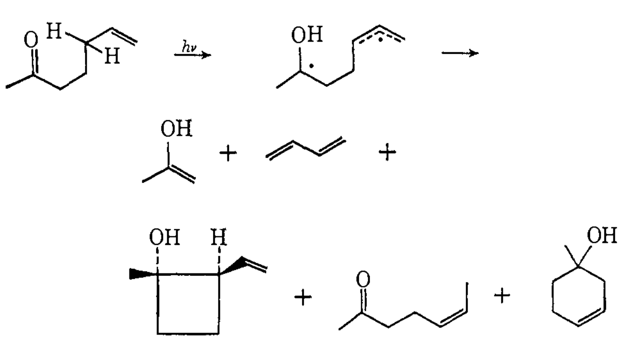
[5] N. C. Yang and S. P. Elliott, *J. Amer. Chem. Soc.*, **90**, 4194 (1968).

[6] The lifetimes of the singlet excited state of acetone, 2-butanone, 3-pentanone, and cyclopentanone, *i.e.*, alkanones without γ hydrogens, range from 1.9 to 4.4 nsec: F. Wilkinson, *Advan. Photochem.*, **3**, 255 (1964).

[7] *cis*-5-Hepten-2-one is probably formed by a sigmatropic rearrangement of *trans*-1-methyl-1-vinylcyclobutanol.

[8] N. C. Yang, A. Morduchowitz, and D. H. Yang, *J. Amer. Chem. Soc.*, **85**, 1017 (1963).

[9] N. C. Yang and E. D. Feit, *ibid.*, **90**, 504 (1968).



photolysis of 2-hexanone-5,5-d_2 is enhanced over 2-hexanone.[10] The quantum yield from the triplet state (ϕ_t) increases from 0.23 to 0.37, while that from the singlet state (ϕ_s) decreases from 0.10 to 0.05. Since the γ hydrogen is 2.7 times more reactive than the γ deuterium in the reactions from the singlet state, deuteration may also decrease the k_{-s} in the deuterated ketone. The ϕ_{st} will increase as the k_s and k_{-s} decrease, and ϕ_t for 2-hexanone-5,5-d_2 increases over that of 2-hexanone due to the increase in ϕ_{st}.

In conclusion, we wish to report that the rate for nonradiative decay from the singlet state (k_{-s}) of alkanones with γ hydrogens increases as the nature of the γ hydrogen changes from primary to secondary to tertiary and that the nonradiative process may involve the reverse chemical reaction from the singlet biradical intermediate. The results of this investigation and our earlier work constitute a complete analysis of the behavior of photoexcited 2-alkanones with γ hydrogens.[10a]

[10] D. R. Coulson and N. C. Yang, *J. Amer. Chem. Soc.*, **88**, 4511 (1966).

[10a] Note Added in Proof. Recent theoretical work by A. Heller, *Mol. Photochem.*, **1**, 257 (1969), suggests that chemical reactions may well be involved in the nonradiative relaxation of excited states. We reach the same conclusion independently and our work is in complete agreement with his theory.

[11] The authors wish to acknowledge the National Science Foundation and the U. S. Public Health Service for the support of this work.

[12] National Science Foundation Trainee, 1966–1968; National Institutes of Health Predoctoral Fellow, 1968–1970.

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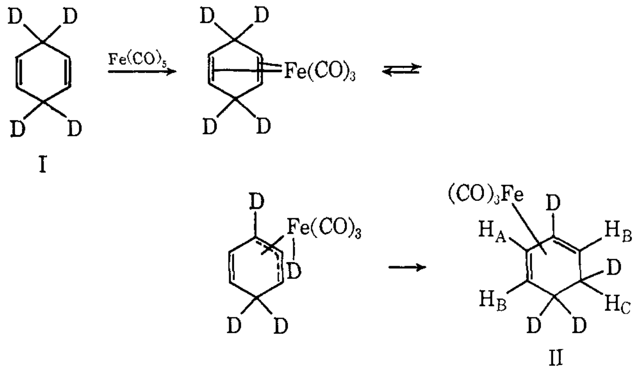
Mechanism of Formation of Conjugated Diene–Iron Tricarbonyl Complexes from Nonconjugated Dienes

Sir:

Reactions of monoolefins with a catalytic amount of iron pentacarbonyl leads to isomerization.[1] Two mechanisms have been proposed for this reaction: an addition–elimination mechanism and a mechanism involving allylic hydrogen abstraction. The iron carbonyl catalyzed isomerization of allylic alcohols to carbonyl compounds has recently been shown to proceed *via* the allylic hydrogen abstraction mechanism.[2,3] To our knowledge, no results have appeared concerning the mechanism of formation of conjugated diene–iron tricarbonyl complexes from nonconjugated dienes, a synthetically important *noncatalytic* reaction.[4,5] This communication reports a mechanistic investigation of the reaction of one such diene, cyclohexa-1,4-diene, with iron pentacarbonyl.

Cyclohexa-1,4-diene reacts with iron pentacarbonyl or triiron dodecacarbonyl to give cyclohexa-1,3-diene-iron tricarbonyl.[4,6] An allylic hydrogen abstraction mechanism has been proposed for this type of reaction.[5,7] A simple approach to this mechanistic problem involves labeling the methylene groups of the diene with deuterium and analyzing for deuterium in the product. 3,3,6,6-Tetradeuteriocyclohexa-1,4-diene (I) was prepared as previously described.[8] A mixture of the deuterated diene and iron pentacarbonyl in anhydrous benzene was photolyzed under conditions identical with those described for the nondeuterated compound.[4] The product, identified as II (described below), was obtained as a yellow oil (bp 77° (0.8 mm)) in 46% yield.



The infrared spectrum (neat) of II showed terminal metal carbonyl stretching bands at 2062 and 1976 cm^{-1} and carbon–deuterium stretching at 2210 and 2190 cm^{-1}. The nuclear magnetic resonance spectrum, recorded in carbon tetrachloride solution with tetramethylsilane as internal standard, gave signals at 1.58, 3.26, and 5.38 ppm in the ratio of 1.0:1.8:1.0 for H_C, H_B, and H_A, respectively. The mass spectrum of cyclohexa-1,3-dieneiron tricarbonyl has been reported.[9] We recorded the mass spectra of both the nondeuterated and deuterated complexes (at 70 eV). The mass spectrum of cyclohexa-1,3-dieneiron tricarbonyl was in agreement with the results of Winters and Kiser, giving a parent molecular ion peak at *m/e* 220. The molecular ion peak of the deuterated complex appeared at *m/e* 224 and the fragmentation pattern, like that of the corresponding nondeuterated complex, was characterized by successive loss of carbon monoxide units from $C_6H_4D_4Fe(CO)_3^+$ to give the ions $C_6H_4D_4Fe(CO)_2^+$ and $C_6H_4D_4Fe(CO)^+$ at *m/e* 196 and 168, respectively. No ion of composition $C_6H_4D_4Fe^+$ was observed (the nondeuterated analog $C_6H_8Fe^+$ was also not detected[9]). However, as $C_6H_6Fe^+$ was abundant in the spectrum of the nondeuterated compound, $C_6H_4D_2Fe(CO)^+$ (*m/e* 164) was in large abundance in the mass spectrum of II (the ion $C_6H_3D_3Fe(CO)^+$ was present in low abundance). Loss of carbon monoxide from $C_6H_4D_2Fe$-

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[1] T. A. Manuel, *J. Org. Chem.*, **27**, 3941 (1962).

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[3] F. G. Cowherd and J. L. von Rosenberg, *J. Am. Chem. Soc.*, **91**, 2157 (1969).

[4] A. J. Birch, P. E. Cross, J. Lewis, D. A. White, and S. B. Wild, *J. Chem. Soc.*, *A*, 332 (1968).

[5] R. Pettit and G. F. Emerson, *Advan. Organometal. Chem.*, **1**, 1 (1964).

[6] J. E. Arnet and R. Pettit, *J. Am. Chem. Soc.*, **83**, 2954 (1961).

[7] R. Pettit, G. F. Emerson, and J. Mahler, *J. Chem. Educ.*, **40**, 175 (1963).

[8] J. R. Campbell, Ph.D. Thesis, Queen's University, 1969; see S. Wolfe and J. R. Campbell, *Chem. Commun.*, 877 (1967).

[9] R. E. Winters and R. W. Kiser, *J. Phys. Chem.*, **69**, 3198 (1965).