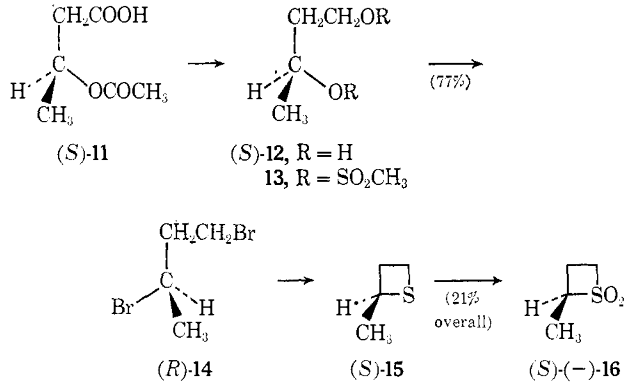
Scheme III



solute configuration of favored enantiomer (+)-**5** produced in the sulfene–enamine condensation is established as *S*.

In light of the above data, it is clear that asymmetric induction in (2 + 2) cycloadditions can be achieved. Attempts to increase the extent of stereoselectivity by structural modification of the amine and other means is presently receiving attention. Discussion of the observed stereoselectivity in terms of transition-state theory is deferred to the full paper.

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Received October 10, 1969

Photochemistry of (*S*)-(+)-5-Methyl-2-heptanone

Sir:

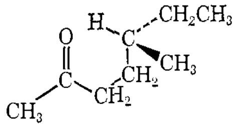
The photochemistry of alkanones with γ hydrogens is interesting from a mechanistic point of view in that their reactions may take place from their singlet state as well as from their triplet state. The reactions proceed with moderate quantum yields, *e.g.*, 0.34 ± 0.01 for 2-hexanone, and the principal products are those derived from the type II process and cyclobutanols. Wagner[1] has suggested that the triplet state of ketones with γ hydrogens will give a biradical intermediate first which may revert to the starting ketone or proceed to give products in nonpolar solvents, while in polar solvents it will proceed to give products predominantly. Therefore, the reactions may involve a vibrationally excited ground state as well. In order to achieve a better understanding of the relative roles of the excited states and the nature of the nonradiative decay processes in the photochemistry of alkanones with γ hydrogens, (*S*)-(+)-5-methyl-2-heptanone (I) was synthesized and its photochemistry investigated.

Table I

Solvent	$\phi_{-\text{ketone}}$	$\phi_{\text{type II}}$	$\phi_{\text{cyclobutanols}}$	$\phi_{\text{racemization}}$	$\phi_{\text{photoreduction}}$
Hexane	0.158 ± 0.003	0.128 ± 0.003	0.025 ± 0.001	0.08 ± 0.02	0.0040 ± 0.0005
t-Butyl alcohol	0.18 ± 0.04	0.157 ± 0.004	0.029 ± 0.002	0.04 ± 0.02	
Hexane + 2.5 *M cis*-1,3-pentadiene	0.073 ± 0.002	0.071 ± 0.002	0.006 ± 0.001	0.002 ± 0.010[a]	$<10^{-4}$ [a]
t-Butyl alcohol + 2.5 *M cis*-1,3-pentadiene	0.07 ± 0.02	0.058 ± 0.001	0.004 ± 0.001		

[a] In 5.0 *M cis*-1,3-pentadiene.

Compound I was synthesized from (*S*)-(+)-1-bromo-3-methylpentane[2] by addition of the corresponding Grignard reagent to acetic anhydride[3] and purified through its semicarbazone to give a product of 99.4% purity as indicated by vpc, bp 77–78° (40 mm), $[\alpha]^{25}\text{D}$ +9.84°, semicarbazone mp 133–134°.



I

As expected, irradiation of I in either hexane or *t*-butyl alcohol in the presence or absence of *cis*-1,3-pentadiene gave acetone, 2-methyl-1-butene, and a mixture of cyclobutanols as the major products. A very small amount of 5-methyl-2-heptanol was also detected when the irradiation was carried out in hexane but not in *t*-butyl alcohol or in hexane with pentadiene. Each solution was 1.0 *M* in I. The irradiating wavelength was 313 nm, carried out on an apparatus previously described.[4] Quantum yields for the disappearance of ketone, the formation of acetone, and the formation of the cyclobutanols were determined using 2-hexanone as a secondary actinometer. Quantum yields for racemization were determined by recovering the irradiated ketone by vpc, measuring the change in optical rotation at four wavelengths between 220 and 305 nm on a Cary 60 spectropolarimeter, and relating the amount of racemate formed to the quantum yield for the disappearance of ketone and the per cent conversion. The results of the irradiation under various conditions are summarized in Table I.

From the results we find two observations interesting. (1) Although the photochemical reactions of I proceed with concurrent racemization in both hexane and *t*-butyl alcohol, the reactions in the presence of pentadiene, *i.e.*, those from the singlet state, do not proceed with racemization. Therefore, the racemization must take place from the triplet state. The results suggest that the reactions from the singlet and the triplet state of I take place *via* different mechanisms. (2) The reactions proceed with higher quantum yields in *t*-butyl alcohol than in hexane, and the increase in quantum yield is the same as the decrease in racemization within experimental error. The combined quantum yields of observed events in *t*-butyl alcohol are about 0.2, which falls far short of 1.0 as found in the case of analogous aromatic ketones.[1]

Our results provide support for Wagner's theory that the ^{3}n,π^* state of I will decay *via* a biradical interme-

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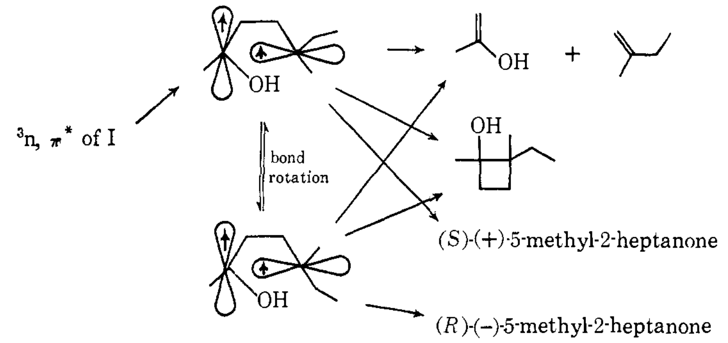
[1] P. J. Wagner, *J. Amer. Chem. Soc.*, **89**, 5898 (1967).

[2] H. S. Mosher and E. La Combe, *ibid.*, **72**, 4991 (1950).

[3] M. S. Newman and W. T. Booth, Jr., *ibid.*, **67**, 154 (1945).

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



(1)

(2)

(3)

(4)

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.

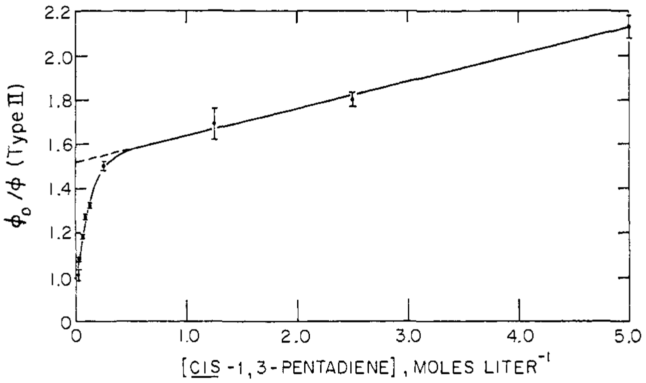


Figure 1.

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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.

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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).