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Katsuyuki Aoki

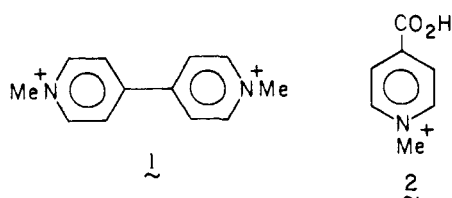
The Institute of Physical and Chemical Research
 Wako-shi, Saitama 351, Japan

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Formation, Trapping, and Lifetime of the Biradicals Generated in the Photochemistry of Valeraldehyde

Sir:

The biradicals produced in the Norrish type II reaction of alkyl aryl ketones have been the subject of a number of studies during the past few years.¹⁻³ Their formation, trapping, lifetimes, and spectral properties are now reasonably understood. The type II process also plays an important role in the photochemistry of aliphatic carbonyl compounds,⁴ but the properties of the intermediate biradicals are largely unknown. The only examples of trapping are those reported by O'Neal for the 2-pentanone-hydrogen bromide system in the gas phase⁵ and by Kusokawa and Anpo⁶ for the interaction of oxygen with the biradicals from 2-pentanone adsorbed on Vycor glass. O'Neal et al.⁵ estimated a biradical lifetime of $\sim 10 \mu\text{s}$ from Stern-Volmer type of studies. No time-resolved experiments have been reported, and, while some of the techniques used for aromatic ketones³ should be applicable to aliphatic carbonyl compounds, the wavelengths of the excitation sources usually employed (nitrogen laser, 337.1 nm, or frequency doubled ruby laser, 347.1 nm) are too long for aliphatic ketones. Aldehydes are slightly red shifted with respect to ketones;⁷ this shift leads to a weak absorption at 337.1 nm, sufficient for adequate excitation.



We have examined the photochemistry of valeraldehyde in the presence of the electron acceptors paraquat (1,1'-dimethyl-4,4'-bipyridylium) ions (**1**) and 4-carboxy-1-methylpyridinium (**2**)⁸ which behave as efficient biradical traps according to reactions 1 and 2, where the asterisk denotes the triplet state, and A is an electron acceptor, **1** or **2**. The formation of $A^{\cdot-}$ can be monitored in time-resolved laser flash

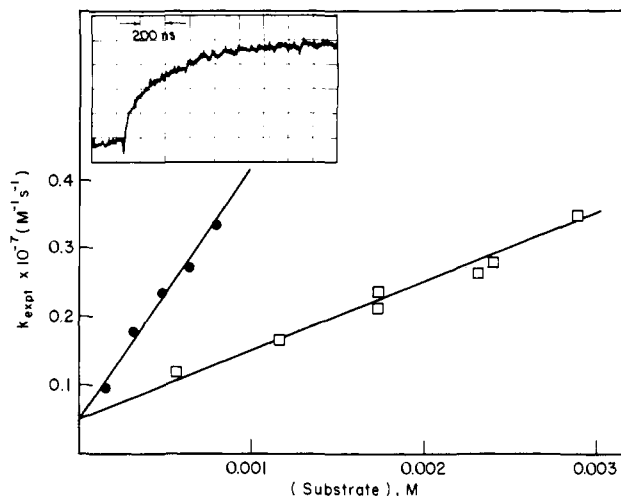
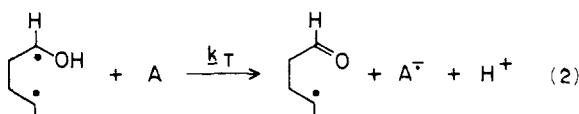
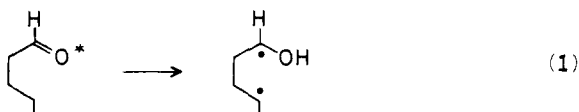


Figure 1. Kinetic data for the trapping of biradicals by **1** (●) and **2** (□) in water-acetonitrile (1:9). Inset: typical time profile for paraquat 0.00064 M. The initial negative signal is due to fluorescence.

photolysis experiments;³ the corresponding time profiles contain information on both, the rate of trapping k_T and the biradical lifetime τ_B . The buildup of $A^{\cdot-}$ follows clean first-order kinetics and the experimental pseudo-first-order rate constants correspond to¹⁰

$$k_{\text{exptl}} = \tau_B^{-1} + k_T[A] \quad (3)$$

Figure 1 shows plots of k_{exptl} vs. $[A]$ for both electron acceptors. As expected, the slope changes, but the intercept is independent of the trapping agent and gives $\tau_B = 2 \mu\text{s}$ in water-acetonitrile (1:9). The rates of trapping are 3.7×10^9 and $1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for **1** and **2**, respectively. Typical aldehyde concentrations were in the 0.35-1.10 M range. The kinetic parameters obtained were independent of this concentration as well as of the light intensity (laser pulses attenuated by a factor of 10).

The assumption and detailed analysis of this type of technique have been reported elsewhere.³ However, it is important to emphasize that the reaction examined involves the biradical rather than the triplet state and that the lifetime of the latter is short compared with τ_B , a critical condition in this type of study. The triplet lifetime of valeraldehyde has been reported as 10 ns in hexane.^{12,13} Further, if at constant paraquat ion concentration one adds a triplet quencher, e.g. *cis*-1,3-pentadiene, the plateau absorbances change, but the kinetics (as measured by k_{exptl}) do not. This is indicative of quenching the precursor of the species leading to $A^{\cdot-}$. In addition, a plot of A_∞^{-1} vs. $[\text{diene}]$, where A_∞ is the plateau absorbance due to $A^{\cdot-}$, is linear and leads to $k_q\tau_T = 350 \text{ M}^{-1}$ from which we estimate a triplet lifetime $\tau_T = 35 \text{ ns}$,¹⁴ which clearly shows that the condition $\tau_T \ll \tau_B$ is fulfilled. Similar experiments with 2-methylpropionaldehyde which has a comparable triplet lifetime but cannot give biradicals did not lead to the formation of $A^{\cdot-}$.

We have also examined samples of matched absorbance and constant paraquat-ion concentration containing valeraldehyde and γ -methylvalerophenone. Examination of the plateau absorbances and using the value of k_T and τ_B for both biradicals, we estimate that the quantum yield of biradical production (triplet derived) from valeraldehyde is $\phi_B = 0.32$ based on the assumption of $\phi_B = 1$ for γ -methylvalerophenone.^{1,4} The value is expected to be lower than unity, reflecting that the quantum yield of intersystem crossing is also < 1 .¹³ It is noteworthy that the signals due to $A^{\cdot-}$ from both **1** and **2** are totally quenchable by dienes, indicating that the biradicals trapped arise exclusively from a triplet state reaction. No evidence for the trapping of singlet-derived biradicals was observed.

Finally, our earlier results³ for aromatic ketones indicated that biradical lifetimes are usually in the 30–100-ns range, while in the case of aliphatic ketones in the gas phase O'Neal et al. reported a value of $\sim 10 \mu\text{s}$.⁵ The results reported in this communication strongly suggest that this difference is real and should be largely attributed to the difference in molecular structure. While it is clear that the lifetimes of simple aliphatic biradicals are substantially longer than those of aromatic ones, the reasons for this difference are as yet unclear. In the case of aromatic biradicals we have proposed that the lifetimes were controlled by intersystem crossing,³ whether this conclusion can be generalized remains to be seen, and it seems certain that the detailed study of a large number of biradical processes will be required before the intricacies of their behavior can be unveiled.

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- (15) The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-1888 from the Notre Dame Radiation Laboratory.

M. V. Encinas, J. C. Scaiano*

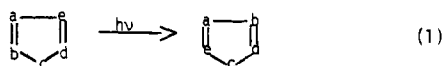
Radiation Laboratory,¹⁵ University of Notre Dame
Notre Dame, Indiana 46556

Received May 16, 1978

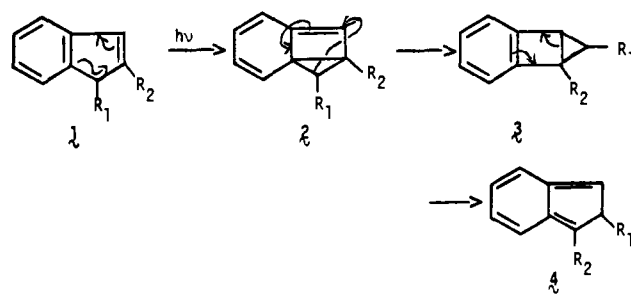
Stereochemistry of the Indene Phototransposition Reaction and the Mechanistic Implications Thereof¹

Sir:

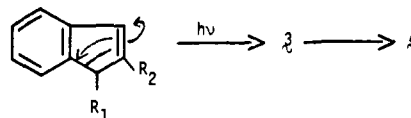
There has recently been considerable interest in phototransposition reactions which have the net effect of interchanging atoms which are 1,3 related within a five-membered ring, i.e. eq 1. Examples have been reported for various heterocycles,² for [¹³C₂]cyclopentadiene,³ and for several alkyl-substituted indenenes.⁴ Two mechanisms will readily accommodate these interconversions—a multistep process involving initial [$\pi^2 + \pi^2$] intramolecular cycloaddition and a "conju-



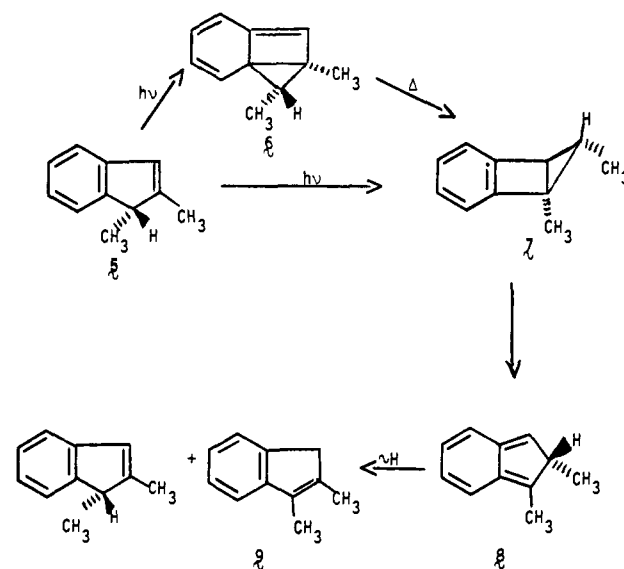
Scheme I. Initial [$\pi^2 + \pi^2$]



Scheme II. "Conjugated Di- π -methane"



Scheme III



gated di- π -methane" rearrangement. These are shown in Schemes I and II as exemplified by the indene rearrangement (the ultimate products from which are a pair of isomeric indenenes resulting from 1,5 hydrogen shifts in the isoindene 4). In both of the above schemes, migration of the central atom is the critical step, and we herein report that, within the indene series, *this migration proceeds with remarkable stereospecificity to give clean inversion at the migrating center.*

Our observation, presented in terms of the two mechanistic options, is shown in Scheme III.⁵ The molecule studied (5) gives rise to a partially degenerate rearrangement with *virtually equal formation of 2,3-dimethylindene (9) and the starting material*. This ratio was determined by photolyzing 1-methyl-2-trideuteriomethylindene. The amount of 9-*d*₃ formed was determined by VPC, and the amount of 1-trideuteriomethyl-2-methylindene (10) was determined by NMR analysis of a VPC-purified mixture of the 1,2-dimethylindene (*d*₃) isomers. The ratio of 10 to 9-*d*₃ was 0.93.

Photolysis of 0.01 M hexane solutions of optically active (S)-(+)-5⁶ to as much as 28% formation of 9 (and therefore $\sim 54\%$ rearrangement) led to only a 1% average change in the specific rotations of 5, measured at nine different wavelengths with a Cary Model 60 spectropolarimeter. Lower conversion runs gave even smaller amounts of racemization; for example, 9.6% formation of 9 is accompanied by 0.06% diminution in rotation of 5! If one assumes that the 1,5 hydrogen shift converting 8 to 5 is suprafacial (the allowed path for this six-