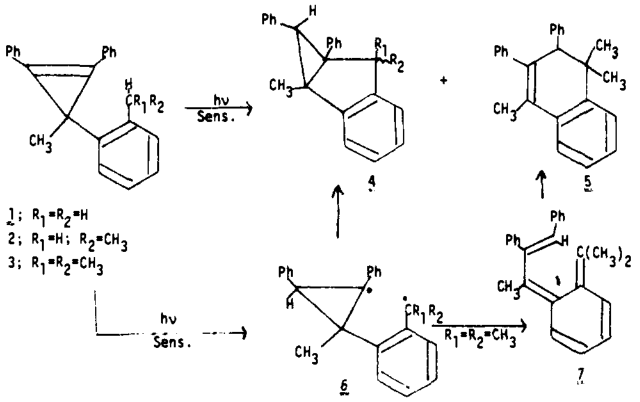
Communications to the Editor

Tunneling Effects in the Hydrogen Atom Transfer Reaction of Tetrasubstituted Cyclopropenes

Sir:

Substitution of hydrogen with deuterium in organic compounds may exert a marked effect on certain properties of their excited states.[1-4] Theory predicts that deuterium should decrease the rate of $T^* \rightarrow S_0$ and $S^* \rightarrow S_0$ radiationless transitions.[5] The extent of the primary deuterium isotope effect will depend on how extensively the C–D bond interacts with the excited state. Deuterium labeling has been widely used in mechanistic studies of the type II photoelimination of ketones.[6-11] Primary kinetic isotope effects have been reported for several ketones with values of k_H/k_D ranging from 0.9 to 5.5[12,13] In previous studies we had reported that the triplet-sensitized irradiation of tetrasubstituted cyclopropenes possessing γ hydrogens leads to products involving intramolecular transfer of the hydrogen atom.[14] In this communication we report on the unusually large primary kinetic isotope effect associated with this reaction.

The triplet-sensitized photobehavior of a number of 3-(*o*-alkyl)phenyl-substituted cyclopropenes was investigated. In each case, products arising from intramolecular hydrogen transfer were observed. The sensitized photolysis of cyclopropene **3** resulted in a 3:2 mixture of **4** and **5**. Hydrogen transfer from the benzylic carbon to the triplet π–π^* excited state of the cyclopropene would be expected to produce biradical **6**. Simple collapse of **6** with carbon–carbon bond formation furnishes benzobicyclohexane **4**. In the case of cyclopropene **3**, the biradical intermediate is long lived enough to undergo cyclopropyl ring opening in competition with coupling. Electrocyclic ring closure of the suspected ring opened species **7** leads to the formation of **5** which has been shown to be a primary photoproduct. Cyclopropenes **1** and **2**, without the added methyl group stabilization, generate a more reactive diradical which rapidly couples before it has a chance to undergo ring opening.



When the sensitized irradiation of an unsymmetrical cyclopropene such as 1,3-diphenyl-2-methyl-3-(*o*-tolyl)cyclopropene (**8**) was carried out in benzene, benzobicyclohexane **9** was isolated as the exclusive photoproduct. No signs of the isomeric benzobicyclohexane **10** could be detected in the crude photolysate. Thus, the reaction is completely stereospecific and involves hydrogen atom transfer to the carbon bearing the methyl group. This is undoubtedly related to the fact that the diradical produced on hydrogen transfer to the methyl-bearing carbon allows maximum delocalization of the radical centers in the resulting diradical intermediate.

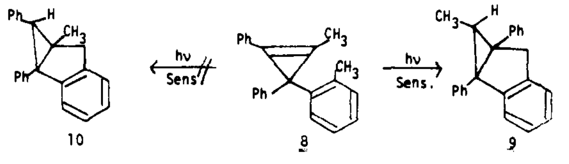
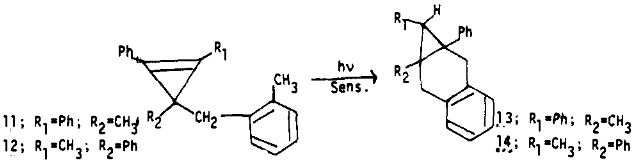


Table I. Quantum Yield and Kinetic Data for the Triplet Sensitized Hydrogen Abstraction Reaction[a,b]

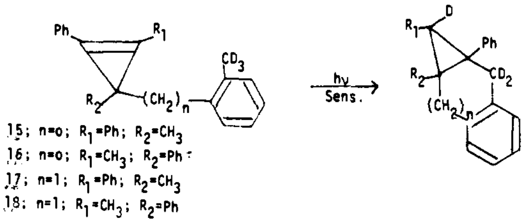
cyclopropene	Φ^c	$k_{CQ}\tau^3{}_C$, M^{-1}	τ, $10^7\ s^{-1}$	k_r, $10^5\ s^{-1}$
1	0.19	4850	9.7	1.96
2	0.68	4200	8.13	8.36
11	0.13	4760	9.52	1.37
15	0.0098	5730	11.5	0.085
17	0.008	5050	10.1	0.079
8	0.56[d]			
16	0.165[d]			
12	0.30[d]			
18	0.091[d]			

[a] Concentration of cyclopropene, ~1 × 10^{-2} M. [b] 40 °C. [c] Sum of all products. [d] 1.5 × 10^{-2} M.

We have also studied the triplet induced photochemistry of the closely related 3-(*o*-alkylbenzyl)-substituted cyclopropene system. The sensitized irradiation of **11** produced **13** in quantitative yield. Similar behavior was observed with the unsymmetrical isomer **12**.



To provide more detailed information concerning the hydrogen transfer reaction, the effect of deuteration upon the rate constant for hydrogen abstraction has been examined. The triplet sensitized photolysis of the deuterated cyclopropenes **15–18** was much slower than that of the undeuterated compounds. Comparative NMR spectra of the deuterated and authentic undeuterated photoproducts indicate that one deuterium atom was present in the expected endo position of the benzobicycloalkane ring.



Recently, Cristol and co-workers have described a method for the treatment of quenching data of photosensitized reactions which allows for the determination of the lifetime of the triplet state.[15] We have used this method to approximate the rate of hydrogen transfer of the triplet state of the symmetrically substituted cyclopropenes. Quantum yields and k_r values are given in Table I for the cyclopropenes studied.[16] With the unsymmetrically substituted cyclopropenes, the quantum yield

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for abstraction was found to depend on the concentration of starting material,[14] and consequently it was not possible to determine the rate of hydrogen transfer by Cristol's method. As may be noted from Table I, the quantum yields for hydrogen transfer decrease substantially with deuterium substitution. The relative lifetime of the triplet states of the deuterated and nondeuterated symmetrical cyclopropenes may be estimated from the relative ratios of the Stern–Volmer slopes.

$$(\Phi_H/\tau_H)(\tau_D/\Phi_D) = k_H/k_D$$

Our work shows that the triplet lifetimes are very similar (ca. within 10%) and consequently the ratio of quantum yields provides a good indication of the magnitude of the primary deuterium isotope effect.[17] The results obtained with the symmetrical cyclopropenes indicate that the deuterium isotope effect for the γ-abstraction reaction corresponds to $k_H/k_D = 23$ for **1** vs. **15** and $k_H/k_D = 17$ for **11** vs. **17**. *The primary isotope effect found with these two systems is significantly larger than any previously reported value for hydrogen transfer to an excited state.* In contrast to the results obtained with **15** and **17**, a much smaller effect on the quantum efficiency of product formation was observed with the unsymmetrical cyclopropenes **16** and **18** (i.e., $k_H/k_D \sim 3.3{:}1$).

The magnitude of the primary isotope effect in a hydrogen-transfer reaction has been suggested to depend on the symmetry of the transition state and is a maximum when the hydrogen is symmetrically bonded to the atoms between which it is being transferred.[18] Calculations of isotope effects for simplified models of hydrogen-transfer reactions are consistent with the conclusion that the isotope effect should pass through a maximum for a symmetrical transition state.[19] Apparently, the transition state for the hydrogen-transfer reaction with cyclopropenes **15** and **17** is very nearly symmetrical and the isotope effect is near the maximum value.[20] A substantial tunnel correction is necessary to reconcile these results with absolute reaction rate theory.[19] Thus, a plausible explanation to account for the large deuterium isotope effect is that the barrier for hydrogen transfer with cyclopropenes **15** and **17** is high and thin, which is the ideal situation for tunneling.[21]

Hammond's postulate suggests that the most symmetrical transition state should occur for that case in which the heat of reaction is most nearly zero.[22] Biradical formation from the symmetrical cyclopropene involves the making and breaking of bonds with similar dissociation energies. With the 1,3-diphenyl-substituted systems, hydrogen abstraction occurs on the methyl-bearing carbon atom and therefore the heat of reaction would be expected to be considerably more exothermic. The greater exothermicity of biradical formation with the unsymmetrical cyclopropenes is in accord with the smaller kinetic isotope effect for hydrogen transfer. In fact, the values obtained ($k_H/k_D \sim 3.3$) correlate well with related results in the literature.[23,24]

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References and Notes

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(16) *trans*-Stilbene (E_T = 50 kcal/mol) was used as the quencher in the Stern-Volmer experiments. It was assumed that both triplets (i.e., thioxanthone (E_T = 65.5 kcal/mol) and cyclopropene ($E_T \sim$ 55 kcal/mol)) were quenched at the same diffusion-controlled rate.
(17) We have previously shown that the initially produced biradical intermediate does not undergo reverse hydrogen transfer[14] as was observed with phenyl alkyl ketones.[12]
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α Deprotonation of β-Lactones—an Example of a "Forbidden" β Elimination

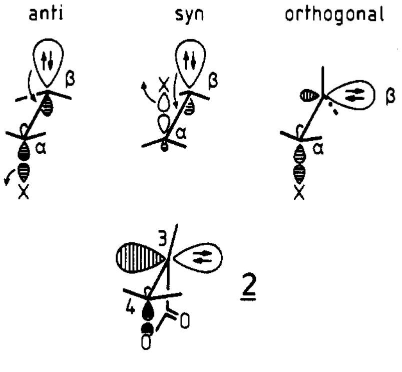
Sir:

The stereochemistry of β eliminations has been investigated extensively for decades;[1] from the data which have thus been accumulated it clearly emerges that β eliminations of any type can only proceed if the electron-donating (β) and the electron-accepting (α) orbital adopt a syn or an anti arrangement. We term these eliminations "allowed". By contrast, the process may be considered "forbidden" if α and β are fixed in a strictly orthogonal position (Chart I). We report here that the 3-deprotonated 2-oxetanones (β-lactones) **2** are surprisingly stable and that an orthogonal orbital arrangement may be held responsible for this phenomenon.

2 was generated by deprotonation of the corresponding β-lactone (2-oxetanone)[2] (**1**) with lithium diisopropylamide in THF at −78 °C (Scheme I); at this temperature **2** remains unchanged and adds a variety of electrophiles at C-3 (Table I).[3] On warming to room temperature the expected β elimination slowly occurs and the acrylic acid anion **5** is formed in quantitative yield.[4] Apparently, the conversion of **1** into **5** represents the first E1cB elimination with an oxygen leaving group in which the carbanion intermediate can be trapped with electrophiles.[5]

The stability of **2** is surprising because β-acyloxy and β-alkoxy carbanions are very liable toward elimination if their *O*-acyl (or *O*-alkyl) moiety is part of a small ring.[6] In fact we

Chart I



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