zene solution, the quantum yield is 200 times smaller[9] ($\Phi = 1.4 \times 10^{-4}$).

Since dimerization is a bimolecular process, increased concentration should increase the quantum yield. Therefore, since both reactions pass through the same triplet, the inefficiency following excitation to S_1 demands that there be an earlier deactivation step by a concentration dependent mechanism.

A similar observation was made with respect to the cycloaddition with ethyl vinyl ether to give the thietane.[3] Both the reaction at 250 nm (quenched with 1,1′-azoisobutane) and that at 500 nm (quenched with 9-methylanthracene[3]) proceed through the same triplet. But at the same olefin (2.0 *M*) and **1** (0.2 *M*) concentration the quantum yields were 1.6×10^{-2} (250 nm) and 4.6×10^{-4} (500 nm), respectively, a ratio of 35.

These observations appear to require the following processes

$$\begin{gathered}
S_0 \xrightarrow{h\nu} S_1 \text{ or } S_2 \\
S_2 \longrightarrow \longrightarrow T_1 \qquad (\Phi_n) \\
S_2 \longrightarrow S_1 \qquad (\Phi_m) \\
S_1 \xrightarrow{k_d} S_0 \\
S_1 \xrightarrow{k_f} S_0 + h\nu' \\
S_1 + S_0 \xrightarrow{k_{sq}} 2S_0 \\
S_1 \xrightarrow{k_{isc}} T_1 \longrightarrow \text{products}
\end{gathered}$$

The quantum yields of triplets (T_1) from excitation to S_2 ($\Phi_{T''}$) and S_1 ($\Phi_{T'}$) are given by the expressions 1 and 2.

$$\Phi_{T''} = \Phi_n + \frac{\Phi_m k_{isc}}{k_d + k_f + k_{isc} + k_{sq}[S_0]} \tag{1}$$

$$\Phi_{T'} = \frac{k_{isc}}{k_d + k_f + k_{isc} + k_{sq}[S_0]} \tag{2}$$

Since the lifetime[4] of T_1 is of the order of 10^{-6} sec it follows that even for the dimerization in dilute solutions ($\geq 10^{-3}$ *M*) essentially all triplets must be trapped since this is occurring at a diffusion-controlled rate.[4] The quantum yields of dimer must then reflect the quantum yields of triplets; *i.e.*, $\Phi_{T''}/\Phi_{T'} = 200$, where $\Phi_{T''}$ is at 6.46×10^{-3} *M* and $\Phi_{T'}$ is at 0.2 *M*. Thus

$$1 + \frac{k_d}{k_{isc}} + \frac{k_f}{k_{isc}} + \frac{k_{sq}[0.2]}{k_{isc}} = \frac{200}{\Phi_{T''}} \tag{3}$$

Similarly, we may obtain for the quantum yield of fluorescence the expression[10,11]

$$1 + \frac{k_d}{k_f} + \frac{k_{isc}}{k_f} + \frac{k_{sq}[5 \times 10^{-3}]}{k_f} = \frac{1}{\Phi_f} \geq 2.7 \times 10^3 \tag{4}$$

Further information is available from cycloaddition studies. Since the yield of triplets at 500 nm (0.2 *M* **1**) is $^1/_{200}$th that at 250 nm, then the quantum yield *per unit triplet, i.e.*, quantum yield of product per molecule in the triplet state, for cycloaddition is given by the expression $(4.6 \times 10^{-4} \times 200)/\Phi_{T''}$. However, both olefin and **1** compete for these triplets, and the competition from the thione may be corrected for.

The usual steady-state treatment for the addition to the olefin gives the expression 5, where $k_{d'}$ is the unimolecular decay rate constant of the triplet, k_{dim} is the rate constant for trapping of the triplet by thione, and k_{cyclo} is the rate constant for trapping by olefin (in concentration [O]).

$$\Phi^{-1} = \text{constant} \times \left\{1 + \frac{k_{d'} + k_{dim}[S_0]}{k_{cyclo}[O]}\right\} \tag{5}$$

A plot of Φ^{-1} against $[O]^{-1}$ gives the intercept and slope from which the parenthetical term in (5) can be extracted. Since $k_{d'}$ and k_{dim} are known from independent experiments[4] the value of $(k_{dim}[S_0]/k_{cyclo}[O])$ at $[S_0] = 0.2$ *M* and $[O] = 2.0$ *M* can be found and has the value 6. This represents the competition for the triplet and so the quantum yield of adduct per unit triplet in the absence of competition by the thione would be seven times larger than $(4.6 \times 10^{-4} \times 200)/(\Phi_{T''})$, *i.e.*, $(0.64/\Phi_{T''})$. This imposes the limits $1 \nless \Phi_{T''} \nless 0.64$ since no quantum yield may exceed unity. Inserting this range of values into eq 3 requires that $(k_{sq}/k_{isc}) \sim 10^3\ M^{-1}$ (where $[S_0] = 0.2$ *M*) since the other terms must be small. Inserting the value of k_f[10] and $[S_0] = 5 \times 10^{-3}$ in eq 4 gives $k_{sq} \sim 10^{10}\ M^{-1}\ \text{sec}^{-1}$, *i.e., that quenching of* S_1 *is near diffusion controlled.*

The same conclusion may be reached by another route. If triplet **1** is trapped by the olefin, and a fraction *p* of the biradical or complex gives product, then the constant in eq 5 may be expressed as shown in eq 6.

$$\left(1 + \frac{k_f}{k_{isc}} + \frac{k_d}{k_{isc}} + \frac{k_{sq}[0.2]}{k_{isc}}\right)p^{-1} = \text{constant} \tag{6}$$

This has, from the intercept of the plot referred to above, a value of 580 ± 80. Since *p* must be close to unity because of the limits set on $\Phi_{T''}$ (and thus of the corresponding value of the quantum yield of adduct per unit triplet, $0.64/\Phi_{T''}$), eq 6 becomes close in value to eq 3, the left-hand terms now being identical.[12,13]

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[9] Irradiation at 500 nm of a solution (1.0 *M*) of **1** in *n*-hexane gave the dimer ($\Phi = 1.7 \times 10^{-4}$). The choice of benzene as solvent was dictated by relative solubility problems for quenching and sensitization studies.

[10] The value of k_f (3×10^4 sec^{-1}) was calculated from the oscillator strength of the absorption band. Φ_f was shown to be less than 3.6×10^{-4} (λ excitation 531 nm; $[S_0] = 5 \times 10^{-3}$ *M*), the lowest detectable level, by comparison with rhodamine B used as a standard.[11]

[11] G. Weber and F. W. J. Teale, *Trans. Faraday Soc.*, **53**, 646 (1957).

[12] Some evidence is available, and will be discussed in our full paper, that at high concentrations of thione at 250 nm an additional mechanism of dimerization may be available.

[13] If intersystem crossing may occur without self-quenching from a high vibrational level of S_1, then we are unable to distinguish such a process from crossing at S_2 by the present experiments.

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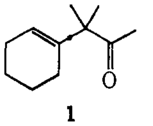
Received March 3, 1973

Evidence for the Existence of a Long-Lived 1,4-Biradical Intermediate in the Intramolecular γ-Hydrogen Abstraction Reaction of β,γ-Unsaturated Ketone Excited Singlet States

Sir:

β,γ-Unsaturated ketones in which competitive intramolecular allylic γ-hydrogen abstraction and α-cleavage photoprocesses are possible have been reported to give good yields of cyclobutanols[1-6] accompanied to a significant extent in acyclic cases by radical coupling products apparently arising from initial α cleavage to acyl and allyl radicals.[1,2] Engel and Schexnayder[6] have very recently shown that the cyclobutanol formation,[7] at least for enone **1**, is an excited singlet-state reaction. There have, however, been no studies to date which allow determination of whether cyclobutanol formation from intramolecular γ-hydrogen abstraction in β,γ-unsaturated ketones is concerted or occurs through the intermediacy of a biradical such as **10**. We would like to report here our results on the photochemistry of β,γ-unsaturated ketones, **2**, **3**, and **4**, which



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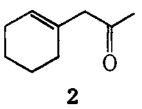

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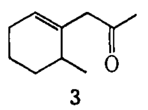

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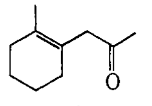

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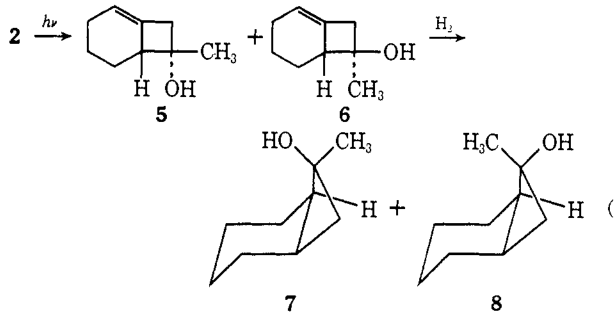
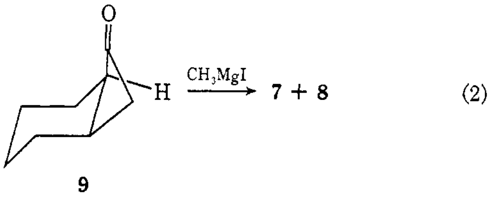
clearly demonstrate the intermediacy of a relatively long-lived 1,4-biradical in cyclobutanol formation from the enone excited singlet state.[8]

Irradiation of a solution of 1-cyclohexenylacetone (**2**) in benzene (1.5 *M*) through quartz using a 450-W medium-pressure mercury lamp for 20 hr gave a 67% yield of two products, **5** and **6**, in a ratio of 2.5:1.0.[9] An identical product ratio was obtained from photolysis of **2** in hexane, although the rate of product formation was slower than in benzene.[10] Nmr, ir, and mass spectra and elemental analyses indicated that both **5** and **6** are unsaturated alcohols isomeric with **2**.[11] The nmr spectra of both products have multiplets (13 H) in the region of δ 1–3 with a sharp singlet (3 H) at δ 1.35 for **5** and 1.17 for **6**.



Catalytic reduction of a 2.5:1 mixture of **5** and **6** over palladium on carbon resulted in formation of two saturated alcohols, **7** and **8**, in a ratio of 2.5:1. These products, **7** and **8**, were shown to be *trans*- and *cis*-7-hydroxy-7-methylbicyclo[4.2.0]octane, respectively, by independent synthesis (eq 2). Addition of methyl magnesium iodide to bicyclo[4.2.0]octan-7-one[12] (**9**) yielded the two cyclobutanols, **7** and **8**, in a 15:1 ratio.[13] It is assumed that the major product, **7**, results from attack of the Grignard reagent on the least hindered side of the bicyclo[4.2.0]octan-7-one.[14] In either conformation, this would result in favored formation of *trans*-7-hydroxy-7-methylbicyclo[4.2.0]octane (**7**). The methyl singlet in the nmr of **7** appears at δ 1.32 while that in **8** is found at δ 1.26 shifted slightly upfield by the increased shielding from the adjacent carbon–carbon bond.[15]



The efficiency of cyclobutanol formation from irradiation of **2** in benzene at 313 nm was measured using benzophenone–benzhydrol actinometry.[16] Quantum yields for formation of **5** and **6** were determined to be 0.055 and 0.02, respectively.

Production of **5** and **6** could occur either in a concerted process or with the intermediacy of the biradical, **10**, obtained by intramolecular hydrogen abstraction from the allylic γ carbon of **2**. If such a biradical intermediate exists and has a sufficiently long lifetime relative to the rate of bond rotation, then one would expect to observe closure at either end of the allylic system. In order to test for the intermediacy of **10** we have studied the photochemistry of 6-methyl-1-cyclohexenylacetone (**3**) and 2-methyl-1-cyclohexenylacetone (**4**).[17] If cyclobutanol formation is concerted then irradiation of **3** should result in formation of only cyclobutanols **11** and **12**, while photolysis of **4** would lead exclusively to **13** and **14**.

Irradiation of a solution of **3** in benzene (0.4 *M*) through quartz yielded three unsaturated cyclobutanols tentatively assigned as **13**, **14**, and **11** or **12**, in a ratio of 7.8:2.4:1.0, as well as **4**. Similar photolysis of **4** gave the same unsaturated alcohols in approximately the same ratio, 7.6:3.5:1.[18] The assignment of the cyclobutanol structures is based on the nmr, ir, and

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

(2) E. F. Kiefer and D. A. Carlson, *Tetrahedron Lett.*, 1617 (1967).

(3) T. Matsui, A. Komatsu, and T. Moroe, *Bull. Chem. Soc. Jap.*, **40**, 2204 (1967).

(4) R. C. Cookson, J. Hudec, A. Szabo, and G. E. Usher, *Tetrahedron*, **24**, 4353 (1968).

(5) R. C. Cookson and N. R. Rogers, *J. Chem. Soc., Chem. Commun.*, 809 (1972).

(6) P. S. Engel and M. A. Schexnayder, *J. Amer. Chem. Soc.*, **94**, 9252 (1972).

(7) We have also observed cyclobutanol formation from photolysis of **1**.

(8) For a preliminary communication of this work, see: H.-F. Chan and J. C. Dalton, Abstracts, 164th National Meeting of the American Chemical Society, New York, N. Y., Sept 1972, ORGN 97.

(9) All product analyses were carried out by glpc using a 10 ft × 0.25 in. or 6 ft × 0.25 in. 6% Carbowax 20M on Chromosorb W 45/60 column.

(10) The faster reaction in benzene may have been due to singlet sensitization by solvent.

(11) Compound **5** has the following properties: oil; mass spectrum (70 eV), *m/e* (rel intensity) 138 (M^+, 11), 95 (99), 67 (50), and 43 (100); ir (CCl_4) 3500, 1615 cm^{-1}; nmr (CCl_4) δ 1.0–2.95 (13 H, m, with singlet at 1.35), 5.3 (1 H, m). **6**: oil; M^+ 138; ir (CCl_4) 3500, 1615 cm^{-1}; nmr (CCl_4) δ 1.0–3.0 (13 H, m, with singlet at 1.17), 5.3 (1 H, m).

(12) L. Ghosez, R. Montaigne, A. Roussel, H. Vanlierde, and P. Mollet, *Tetrahedron*, **27**, 615 (1971).

(13) **7**: oil; mass spectrum (70 eV), *m/e* (relative intensity) 140 (M^+, 3), 97 (20), 59 (100); ir (CCl_4) 3550 cm^{-1}; nmr (CCl_4) δ 0.8–1.2 (15 H, m, with singlet at 1.32), 2.54 (1 H, s, varies with concn). **8**: oil; mass spectrum 140 (M^+, 3), 97 (17), 59 (100); ir (CCl_4) 3550 cm^{-1}; nmr (CCl_4) δ 1.0–1.5 (15 H, m, with singlet at 1.26), 2.8 (1 H, s, varies with concn).

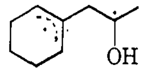
(14) See, for example, A. V. Kamernitzky and A. A. Akhrem, *Tetrahedron*, **18**, 705 (1962).

(15) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Oxford, 1969, Chapter 3-8.

(16) W. M. Moore and M. Ketchum, *J. Amer. Chem. Soc.*, **84**, 1368 (1962).

(17) Compounds **3** and **4** were prepared by reaction of methyllithium with the appropriate carboxylic acid or nitrile.

(18) Ketones **3** and **4** do not photoequilibrate under the conditions of the experiment.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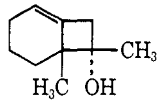
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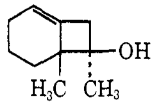
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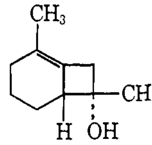
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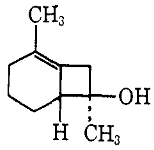
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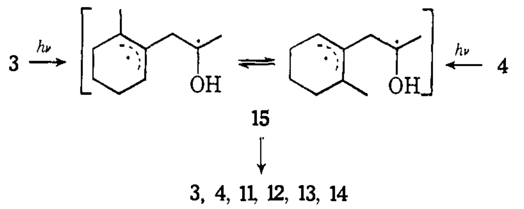
mass spectra.[19] The nmr of **13** and **14** show no vinyl hydrogens, while the third product has absorpion for one vinyl hydrogen at δ 5.3. Each product has two methyl singlets in the nmr with the position being as follows: for **13**, δ 1.52 and 1.35; for **14**, 1.52 and 1.14; and for **11** or **12**, 1.35 and 1.18. The 1.52 singlet in **13** and **14** is assigned to the vinylic methyl. The structures of compounds **13** and **14** are then assigned on the basis of the upfield shift of the remaining CH_3 singlet in **14** relative to **13**, in analogy with the chemical shifts for the methyls in **5** and **6**.

The production of nearly identical ratios of the three cyclobutanols upon photolysis of both **3** and **4**[18] clearly rules out a concerted mechanism for cyclobutanol formation and requires the intermediacy of a biradical, **15**, whose lifetime is long relative to the rate of rotation about the β bond (see eq 3).



(3)

This leaves the question of whether the intramolecular hydrogen abstraction is occurring from the excited singlet or the excited triplet state of these β,γ-unsaturated ketones. Irradiation of a benzene solution (0.5 *M*) of **2** at 313 nm with added 1,3-pentadiene (1 *M*) resulted in no quenching of cyclobutanol formation, suggesting that the reaction occurs either from the singlet state or from a short-lived triplet state.[20] Irradiation of solutions (0.5 *M*) of **2** and **4** in acetone at 313 nm yielded mostly polymer and only small amounts of cyclobutanols. The sensitized product ratios differed from those in the direct irradiation, implying that in the direct irradiation cyclobutanol formation is occurring predominantly through the excited singlet state in analogy with the results of Engel and Schexnayder.[6] This interpretation is further verified by our observation that the fluorescence efficiencies of **2**, **3**, and **4** are all very low, at leat ten times lower than that of methyl allyl ketone, a β,γ-unsaturated ketone containing no allylic γ hydrogens.

Thus, we conclude that cyclobutanol formation is occurring from the n,π^* excited singlet state of β,γ-unsaturated ketones **2**, **3**, and **4** with the intermediacy of a relatively long-lived biradical, **15**. This is quite different behavior from that observed for intramolecular γ-hydrogen abstraction reactions from the S_1 state of saturated alkanones for which the evidence to date rules out a biradical intermediate with a lifetime long relative to the time required for bond rotation[21,22] although there is some evidence that relatively short-lived biradical intermediates may exist.[21b,c] It may be that allylic stabilization of the biradical generated from β,γ-unsaturated ketones leads to a substantial increase in its lifetime.[23]

Acknowledgments. The authors wish to make acknowledgment to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Hoffmann-La Roche Foundation for partial support of this research.

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[19] **13**: oil; mass spectrum (70 eV), *m/e* (relative intensity) 152 (M^+, 9), 109 (100), 67 (45), 43 (61); ir (CCl_4) 3500, 1670 cm^{-1}; nmr (CCl_4) δ 1.0–2.25 (13 H, m, with singlets at 1.35 and 1.52), 2.52 (3 H, m). **14**: oil; mass spectrum 152 (M^+, 11), 109 (100), 67 (46), 43 (53); ir (CCl_4) 3500, 1670 cm^{-1}; nmr (CCl_4) δ 0.9–2.2 (12 H, m, with singlets at 1.14 and 1.52), 2.6 (3 H, m), 2.8 (1 H, s, OH). **11** or **12**: oil; mass spectrum 152 (M^+, 7), 109 (100), 67 (39), 43 (81); ir (CCl_4) 3500, 1660 cm^{-1}; nmr (CCl_4) δ 1.0–2.8 (14 H, m, with singlets at 1.18 and 1.35), 4.55 (1 H, s), 5.3 (1 H, m).

[20] The lack of 1,3-pentadiene quenching also rules out any triplet sensitization by benzene.

[21] (a) N. C. Yang and S. P. Elliott, *J. Amer. Chem. Soc.*, **91**, 7550 (1969); (b) L. M. Stephenson, P. R. Cavigli, and J. L. Parlett, *ibid*,, **93**, 1984 (1971); (c) C. P. Casey and R. A. Boggs, *ibid*., **94**, 6457 (1972).

[22] In the saturated alkanones the bond rotation is around the β,γ-carbon–carbon bond, while in our case it is around the α,β-carbon–carbon bond. The rates of bond rotation may not be the same in both cases; see L. M. Stephenson and T. A. Gibson, *J. Amer. Chem. Soc.*, **94**, 4599 (1972).

[23] The allylic biradical generated by intramolecular γ-hydrogen abstraction from a δ,ϵ-unsaturated ketone, however, appears to undergo closure faster than bond rotation; see K. H. Schulte-Elte and G. Ohloff, *Tetrahedron Lett.*, 1143 (1964); and N. C. Yang, S. P. Elliott, and B. Kim, *J. Amer. Chem. Soc.*, **91**, 7551 (1969).

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Received February 21, 1973

Reversible Binding of Nitric Oxide and Carbon Monoxide to Iron Porphyrins. Assessment of the Role of the Protein in Hemoglobin

Sir:

Iron porphyrins provide one model for the active heme group in hemoglobin (Hb). However, the porphyrins differ in some important respects from the active site in hemoglobin. In the deoxy protein the iron exists as five-coordinate high-spin Fe(II) which reversibly binds one molecule of O_2 per iron.[1] Outside the protein, six-coordinate low-spin Fe(II) porphyrins may be obtained;[2,3] these do not bind oxygen reversibly but rather are rapidly oxidized to Fe(III) in aqueous media.[4–6] While iron porphyrins do not bind O_2 reversibly, we find that they do bind NO and CO reversibly. The binding of CO to heme has been reported in aqueous solution,[7] and the influence of pyridine on the extent of CO binding has been described.[8] The only report of the interaction of NO with hemes

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[1] R. E. Dickerson and I. Geis, "The Structure and Action of Proteins," Harper and Row, New York, N. Y., 1969, p 50.

[2] S. J. Cole, G. C. Curthoys, E. A. Magnusson, and J. N. Phillips, *J. Amer. Chem. Soc.*, **93**, 2153 (1971).

[3] J. P. Collman and C. A. Reed, *ibid.*, **95**, 2048 (1973).

[4] O. H. Kao and J. H. Wang, *Biochemistry*, **4**, 342 (1965).

[5] J. O. Alben, W. H. Fuchsman, C. A. Beaudreau, and W. S. Caughey, *ibid.*, **7**, 624 (1968).

[6] E. B. Fleischer, J. M. Palmer, T. S. Srivastava, and A. Chatterjee, *J. Amer. Chem. Soc.*, **93**. 3162 (1971), and references therein.

[7] J. H. Wang, A. Nakahara, and E. B. Fleischer, *ibid.*, **80**, 1109 (1958).

[8] A. Nakahara and J. H. Wang, *ibid.*, **80**, 6526 (1958).