for B-5–B-10 and B-7–B-8, respectively. Average values for the B–H bond distances of 1.1 and 1.3 Å for terminal and bridging hydrogen atoms, respectively, are consistent with values from other boranes.[7] Each boron atom is six-coordinate, and B-5 is coordinated to boron atoms only. In the n-$B_{18}H_{22}$ molecule[6b] there are two boron atoms each surrounded by six boron atoms; however, these atoms also participate in bridge hydrogen bonding and are thus seven-coordinate.

The $B_{16}H_{20}$ molecule is highly relevant to the chemistry of the $B_{10}H_{14}$, n-$B_{18}H_{22}$, and i-$B_{18}H_{22}$ molecules.[4,6,7] Both $B_{10}H_{14}$ and n-$B_{18}H_{22}$ are products of the same reaction which produces $B_{16}H_{20}$, and $B_{16}H_{20}$ reacts[1] with dimethyl sulfide and triphenylphosphine to yield $B_{10}H_{14}$. In addition, the formal removal of B-9′ and B-10′ from *either* n-$B_{18}H_{22}$ or i-$B_{18}H_{22}$, followed by minor shifts of boron atoms and appropriate rearrangement of bridge hydrogen atoms, yields the $B_{16}H_{20}$ molecule.

Full details of the structural study, as well as chemical implications of the results, will be published in the near future.

Acknowledgment. We thank Dr. Plešek and Dr. Heřmánek for the sample and the Faculty Research Funds of Oakland University and Wayne State University for financial support. We gratefully acknowledge the contribution of the Wayne State University Computing Center.

[7] W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963.

Lawrence B. Friedman
Department of Chemistry, Oakland University
Rochester, Michigan 48063

Richard E. Cook, Milton D. Glick
Department of Chemistry, Wayne State University
Detroit, Michigan 48202

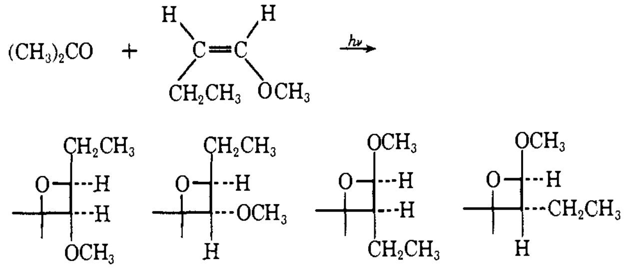
Received September 27, 1968

Molecular Photochemistry. X. The Photocycloaddition of Acetone to 1-Methoxy-1-butene. A Comparison of Singlet and Triplet Mechanisms and Biradical Intermediates[1]

Sir:

The photocycloaddition of ketones to ethylenes has attracted considerable synthetic[2] and mechanistic[3] attention recently. Although triplet ketones are generally the chemically active states in these reactions,[3] cases are now known in which the ketone singlets initiate attack on the ethylene.[3b,e,f] To date, however, there have been no studies which answer the questions: (a) What are the relative reactivities[4] of the S_1 and T_1 states of a given ketone toward a single olefin? (b) What effect, if any, will spin differences have on attack of an excited ketone on an ethylene? (c) If biradical intermediates[5] are formed by attack of S_1 and T_1 on an ethylene, are these intermediates different or comparable in their structures and chemical properties? The last question is particularly intriguing because it examines the nature of spin correlation (spin memory) in a 1,4 biradical, a problem of considerable theoretical[6] and practical[7] interest since, if spin inversion is slow relative to competing processes, biradicals of different multiplicities may exhibit different chemistry.

The photoaddition of acetone to *cis*-1-methoxy-1-butene (*c*-**1**) discussed below appears to be a particularly attractive case to study in order to answer questions a–c. Both S_1 (n,π^*) and T_1 (n,π^*) states of acetone (*vide infra*) attack *c*-**1** to produce[8] the isomeric oxetanes **2–5**. In order to simplify analyses, **4** and **5** were conveniently eliminated by treatment of the photolysate with dilute (0.01 *M*) HCl.[9] The ratio and absolute yields of **2** and **3** were then able to be determined accurately. Stern–Volmer plots of ϕ^0/ϕ for the formation of **2** and **3** *vs.* 1,3-pentadiene (**6**) are shown in Figure 1. At low concentrations of **6** these plots yield a straight line with a slope of 126 and a limiting ratio of **2**:**3** of 1.1. However, at high concentrations of **6** the ratio of **2**:**3** steadily increases and then reaches a limit of 4.1. *The same limiting ratio is approached as the concentration of c-***1** *is increased.* A Stern–Volmer plot ($1/\Phi_2$ *vs.* $1/[c\text{-}\mathbf{1}]$) of the quantum yield for the formation of **2** as a function of *c*-**1** in the presence of 0.3 *M* **6** yields a straight line with a slope of 142 and an intercept of 75. (Preliminary results



2 **3** **4** **5**

---

[1] (a) The authors gratefully acknowledge support of this work by the Air Force Office of Scientific Research (Grant AFOSR-68-1381). We also thank the Ciba Co. for a genrous gift. (b) Part IX: N. J. Turro and R. Engel, *Molecular Photochem.*, in press.

[2] Reviews: L. L. Muller and J. Hamer, "1,2-Cycloaddition Reactions," Interscience Publishers, New York, N. Y., 1967, p 111; D. R. Arnold, *Advan. Photochem.*, **6**, 301 (1968).

[3] (a) N. C. Yang, J. I. Cohen, and A. Shani, *J. Am. Chem. Soc.*, **90**, 3264 (1968); (b) N. C. Yang and R. L. Loeschen, *Tetrahedron Letters*, 2571 (1968); (c) N. C. Yang, R. Loeschen, and D. Mitchell, *J. Am. Chem. Soc.*, **89**, 5465 (1967); (d) N. C. Yang, *Pure Appl. Chem.*, **9**, 591 (1964); (e) N. J. Turro, P. A. Wriede, and J. C. Dalton, *J. Am. Chem. Soc.*, **90**, 3274 (1968); (f) N. J. Turro, P. Wriede, J. C. Dalton, D. Arnold, and A. Glick, *ibid.*, **89**, 3950 (1967); (g) H. Gotthard, R. Steinmetz, and G. S. Hammond, *J. Org. Chem.*, **33**, 2774 (1968); (h) S. Toki and H. Sakurai, *Bull. Chem. Soc. Japan*, **40**, 2889, 4119 (1967); (i) L. A. Singer and G. A. Davis, *J. Am. Chem. Soc.*, **89**, 158, 941 (1967); (j) D. R. Arnold, R. L. Hinman, and A. H. Glick, *Tetrahedron Letters*, 1425 (1964); (k) N. C. Yang, M. Nussim, M. J. Jorgenson, and S. Murov, *ibid.*, 3657 (1964); (l) L. A. Singer and P. D. Bartlett, *ibid.*, 1425 (1964).

[4] Direct measurement of comparative bimolecular reactivities of S_1 and T_1 of alkyl ketones have not been previously measured. See, however, ref 1a and 11 for related studies.

[5] Biradical intermediates have long been assumed to be intermediates in the photocycloaddition of ketones to olefins, but only recently[3e] has this point been examined experimentally; for a review see ref 2 and N. J. Turro, "Molecular Photochemistry," W. A. Benjamin Co., New York, N. Y., 1965, p 208.

[6] For theoretical work on the related trimethylene biradical see R. Hoffmann, *J. Am. Chem. Soc.*, **90**, 1475 (1968); W. B. DeMore and S. W. Benson, *Advan. Photochem.*, **2**, 219 (1964); P. P. Gaspar and G. S. Hammond in "Carbene Chemistry," W. Kirmse, Ed., Academic Press, New York, N. Y., 1964, p 235.

[7] P. D. Bartlett, *Science*, **159**, 833 (1968); P. D. Bartlett, R. Helgeson, and O. A. Wersel, *Pure Appl. Chem.*, **16**, 187 (1968); P. D. Bartlett and N. A. Porter, *J. Am. Chem. Soc.*, **90**, 5317 (1968).

[8] Compounds **2–4** were unambiguously identified from spectral data. The assignments of stereochemistry in **2** and **3** are made on the basis of the nmr coupling constants of the ring hydrogen (J = 6.5 and 5.5 Hz, respectively) and the correlation of the stereospecific singlet addition of acetone to *c*-**1** and *t*-**1** with predominant formation of **2** and **3**, respectively.

[9] Compound **5** elutes with **3** during vpc analysis. Compounds **2** and **3** were totally unaffected by the addition of a trace of HCl.

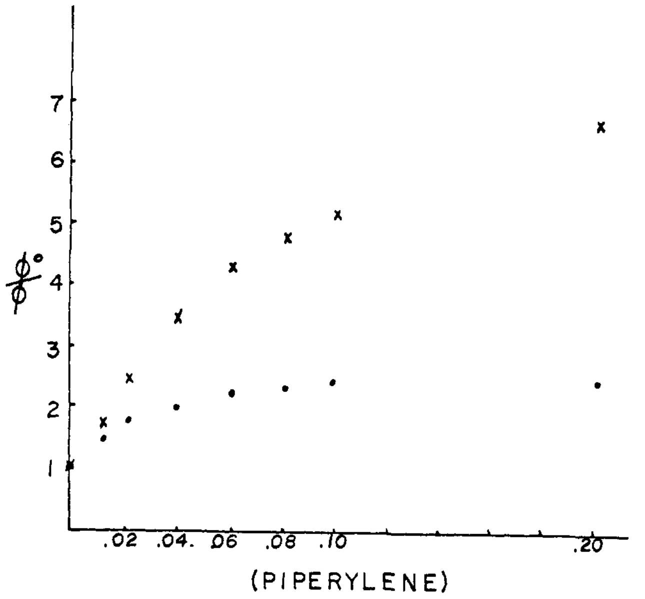


Figure 1. Quenching of oxetane formation by 1,3-pentadiene: ●, isomer 2; X, isomer 3.

indicate that *trans*-1-methoxy-1-butene (*t*-**1**) shows similar behavior.) *cis–trans* isomerization[10] of *c*-**1** to *t*-**1** competes with the cycloaddition reaction. Finally, the ratio (**2** + **3**):(**4** + **5**) is 1.4 for *both* singlet and triplet additions.

In the presence of 0.3 *M* **6** only singlet acetone (A_1) reacts with *c*-**1**, since **6** quenches acetone triplets (A_3) at close to the rate of diffusion[11] and the quenching of acetone triplets by *c*-**1** is at least 100 times less efficient (Figure 1). At low concentrations (*i.e.*, <0.1 *M*) of *c*-**1** in the absence of **6**, essentially only A_3 reacts with *c*-**1** because intersystem crossing is fast enough to compete with singlet cycloaddition. We may thus associate the initial slopes of Figure 1 with k_q^3/k_1^3, so that $k_1^3 = 2 \times 10^8$ l./mol sec.

$$A_3 + \mathbf{6} \xrightarrow{k_q^3} A_0$$

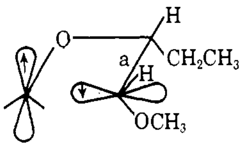
$$A_3 + c\text{-}\mathbf{1} \xrightarrow{k_1} \text{products and quenching}$$

In addition, a plot of $1/\Phi_2$ *vs.* $1/c$-**1** shows that $k_1^1/k_{st} = 0.53$, or $k_1^1 = 2 \times 10^8$ l./mol sec.

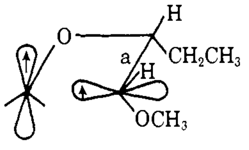
$$A_1 + c\text{-}\mathbf{1} \xrightarrow{k_1^1} \text{products and quenching}$$

$$A_1 \xrightarrow{k_{st}} A_3$$

The similarity of k_1^1 and k_1^3 and the increased stereospecificity associated with singlet addition imply a similar rate-determining attack by A_1 and A_3 on *c*-**1**, to form different intermediates, B_1 and B_3. Furthermore, although the stereospecificity which occurs at high [*c*-**1**] might suggest a precomplex of A_1 and *c*-**1**, *the fact that the same stereospecificity is observed at low* *c*-**1** *when* **6** *is present* eliminates such a complex from consideration. Since the n orbital[3e] should direct an electrophilic attack of either A_1 or A_3 on the electron-rich C=C bond of *c*-**1**, we propose the shown structures for B_1 and B_3 immediately after their formation. B_3 cannot collapse to products without undergoing spin inversion; as a result, rotation around bond a is sufficiently fast relative to closure that essentially no



B_1



B_3

specificity is observed with respect to formation of **2** and **3**. B_1, on the other hand, may be an example of a "virtual biradical," *i.e.*, a biradical for which there may be sufficient bonding between the spin-paired but spatially separated electrons so that rotation is hindered or is slow relative to closure,[12] and, as a result, **2** is formed preferentially to **3**. Our results provide, for the first time, evidence of the comparative chemical behavior of a singlet and triplet 1,4 biradical which have similar and deducible geometry. Interestingly, these results imply that spin correlation between the electrons of 1,4 biradicals is sufficiently strong to affect the chemistry of these species.[13]

---

[10] The mechanism of this reaction is presently under investigation.

[11] P. J. Wagner, *J. Am. Chem. Soc.*, **89**, 2503 (1967); N. C. Yang and S. P. Elliott, *ibid.*, **90**, 4194 (1968).

[12] J. D. Roberts and C. M. Sharts, *Org. Reactions*, **12**, 9 (1962); see also E. F. Kieffer and M. Y. Okamura, *J. Am. Chem. Soc.*, **90**, 4187 (1968).

[13] (a) For related work on 1,4 biradicals see ref 7 and L. K. Montgomery, K. Schueller, and P. D. Bartlett, *J. Am. Chem. Soc.*, **86**, 622 (1964); (b) for recent studies directed toward the observation of differences which might result from radical pairs in solution which have their spins paired or unpaired, see J. R. Fox and G. S. Hammond, *ibid.*, **86**, 4031 (1964); S. F. Nelson and P. D. Bartlett, *ibid.*, **88**, 143 (1966); P. D. Bartlett and J. M. McBride, *Pure Appl. Chem.* **15**, 89 (1967); M. C. R. Symons, *Nature*, **213**, 1226 (1967).

[14] Alfred P. Sloan Fellow, 1966–1970.

[15] National Institutes of Health Trainee, 1965–1966.

Nicholas J. Turro,[14] Peter A. Wriede[15]
Department of Chemistry, Columbia University
New York, New York 10027

Received August 21, 1968

The Absolute Conformation of Chymotrypsin-Bound Substrates. Specific Recognition by the Enzyme of Biphenyl Asymmetry in a Constrained Substrate

Sir:

We submit an experimental solution to the problem of the conformation of α-chymotrypsin-bound (CT-bound) substrates possessing the natural L-phenylalanine pattern of structure.[1–7]

Our approach was facilitated by the discovery of an absolute specificity of CT toward a unique conformer of the 2,2′-bridged biphenyl analog (VI) of benzoylphenylalanine methyl ester ($BzPheOCH_3$), synthesized according to I → VI.

Treatment of diphenic anhydride with $NaBH_4$ in DMF[8,9] afforded the lactone I (87%), mp 136–137°.

---

[1] B. F. Erlanger, *Proc. Natl. Acad. Sci. U. S.*, **58**, 703 (1967).

[2] G. E. Hein and C. Niemann, *ibid.*, **47**, 1341 (1961).

[3] E. S. Awad, H. Neurath, and B. S. Hartley, *J. Biol. Chem.*, **235**, PC35 (1960).

[4] S. G. Cohen and R. M. Schultz, *ibid.*, **57**, 243 (1967).

[5] I. B. Wilson and B. F. Erlanger, *J. Am. Chem. Soc.*, **82**, 6422 (1960).

[6] M. S. Silver and T. Sone, *ibid.*, **89**, 457 (1967).

[7] W. B. Lawson, *J. Biol. Chem.*, **242**, 3397 (1967).

[8] Abbreviations: DMF = dimethylformamide; EEDQ = N-ethoxycarbonyl-2-ethoxy-1,2-dihydroquinoline.[11]

[9] B. Belleau and J. Puranen, *Can. J. Chem.*, **43**, 2551 (1965).