Therefore, the formation of electronically excited photoproducts is highly improbable, based on energetic considerations.

Similar calculations on butyrophenone and its photoproducts gave analogous results except that the biradical is 67 kcal/mole above the butyrophenone ground

state. Formation of the biradical from butyrophenone triplet is thus calculated to be *exothermic* by several kilocalories per mole. This is not in accord with the experimental results of Pitts[9] and Barltrop;[8] however, it should be noted that these calculations do not take conformational factors into account.

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

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Abstract: The photocycloaddition of acetone to *trans*-1-methoxy-1-butene (2) and *cis*-1-methoxy-1-butene (3) has been studied in detail. Four isomeric oxetanes (4, 5, 6, and 7) are formed in good yield. Sensitized *cis-trans* isomerization of the butene also occurs. Kinetic analysis and quantum yield studies reveal that both acetone singlets and acetone triplets are involved in oxetane formation. The stereochemistry of the initial butene is partially retained in the isomeric oxetanes when acetone singlets attack 2 or 3, but is almost completely scrambled when acetone triplets attack 2 or 3. The rate constants for attack of acetone singlets or triplets on a given butene are nearly equal. In addition, the selectivity of attack is the same for attack by acetone singlets or triplets on C_1 and C_2 of a given butene. These results are interpreted in terms of reaction of acetone excited states on methoxybutene to yield singlet or triplet biradical intermediates, depending on the spin state of the attacking acetone molecule. Our results are considered in light of other work on oxetane formation and 1,4 biradicals, and the mechanism of sensitized *cis-trans* isomerization of 2 and 3 is briefly discussed.

The photocycloaddition of ketones to olefins (the Paterno–Buchi reaction)[4] to form oxetanes was discovered at the turn of this century.[5] Although development was slow, recent study has shown the reaction to be synthetically useful.[4] The reaction[4] is known to occur also with olefins and aldehydes, quinones, α-diketones, α,β-unsaturated ketones, α-keto esters, and acyl cyanides.

In general, triplet ketones are the chemically active species[4,6] in the Paterno–Buchi reaction, although cases are now known for which ketone singlets[7] initiate attack

on the ethylene. For the case of electron-rich olefins (alkenes and alkoxylethylenes) the reaction is believed to involve electrophilic attack by the n,π* triplet ketone state to generate preferentially the most stable of the possible biradical intermediates formed by addition of carbonyl oxygen to the carbon–carbon double bond.[8] These conclusions are derived from the following evidence: (a) the stereochemistry of the major oxetane adduct is predicted from Markovnikov addition (which generally also results in formation of the most stable biradical intermediate);[9] (b) the cycloaddition is retarded by triplet quenchers;[10] (c) ketones which undergo efficient photochemical reduction through the n,π* triplet also add efficiently to olefins;[6a,11] (d) the stereochemistry of the oxetanes formed is scrambled and essentially the same mixture of isomeric oxetanes is formed starting with either *cis* or *trans* olefin.[7b]

During the last few years considerable effort has been directed toward the elucidation of the mechanism of photocycloaddition of aryl carbonyl compounds to olefins,[6] but relatively little quantitative work on the addition of alkyl ketones to olefins has been reported.

(1) (a) Molecular Photochemistry. Part XXI. Paper XX: N. J. Turro and T. J. Lee, *J. Am. Chem. Soc.*, 91, 5651 (1969). (b) The authors wish to thank the Air Force Office of Scientific Research (Grants AFOSR-1000-66 and AFOSR-1381-68) for their generous support of this work. The support of the National Science Foundation (Grant NSF-GP-4280) is also gratefully acknowledged; (c) for a preliminary communication of this work, see N. J. Turro and P. A. Wriede, *J. Am. Chem. Soc.*, 90, 6863 (1968).

(2) Alfred P. Sloan Fellow.

(3) National Institutes of Health Trainee, 1965–1966.

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

(5) E. Paterno and G. Chieffi, *Gazz. Chim. Ital.*, 39, 341 (1909); G. Buchi, C. G. Inman, and E. S. Lipinsky, *J. Am. Chem. Soc.*, 76, 4327 (1954).

(6) (a) D. R. Arnold, R. H. Hinman, and A. H. Glick, *Tetrahedron Letters*, 1425 (1964); (b) N. C. Yang, R. Loeschen, and D. Mitchell, *J. Am. Chem. Soc.*, 89, 5465 (1967); (c) J. S. Bradshaw, *J. Org. Chem.*, 31, 237 (1966); (d) R. Srinivasan and K. A. Hill, *J. Am. Chem. Soc.*, 88, 3765 (1966).

(7) (a) N. J. Turro, P. A. Wriede, and J. C. Dalton, *ibid.*, 90, 3274 (1968); (b) N. J. Turro, P. A. Wriede, J. C. Dalton, D. Arnold, and A. Glick, *ibid.*, 89, 3950 (1967); (c) L. A. Singer, G. A. Davis, and V. P. Muralidharan, *ibid.*, 91, 897 (1969); (d) N. C. Yang and R. L. Loeschen, *Tetrahedron Letters*, 2571 (1968); (e) N. C. Yang, *Photochem. Photobiol.*, 7, 767 (1968).

(8) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, p 209.

(9) Exceptions to this rule imply a change in mechanism from electrophilic attack by the n,π* ketone triplet on the C=C bond.[7a,b] For example, see J. A. Barltrop and H. A. J. Carless, *Tetrahedron Letters*, 3901 (1968).

(10) In only a few cases,[1a,7] however, has the occurrence of singlet reactivity been specifically looked for.

(11) The use of photochemical efficiency (quantum yield) as a guide to excited state reactivity is particularly hazardous and often misleading as has been often pointed out: N. J. Turro, *J. Chem. Educ.*, 44, 536 (1967).
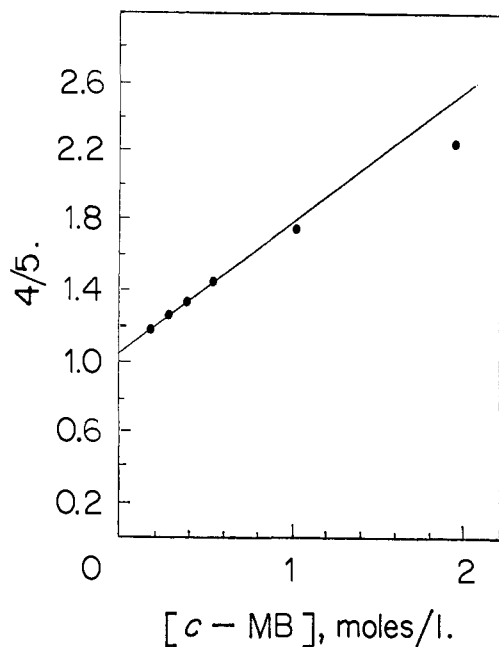
$(CH_3)_2CO$ + CH_3O—C=C—H / H C_2H_5 (structure **2**)

1   **2**

$\downarrow h\nu$

(structures **4**, **5**, **6**, **7** — oxetanes)

CH₃ / O—CH₃ / C_2H_5— —OCH₃ / H   H   **4**

+

CH₃ / O—CH₃ / H— —OCH₃ / H_5C_2 H   **5**

+

CH₃ / O—CH₃ / H— —H / OCH₃ C_2H_5 **6**

+

CH₃ / O—CH₃ / H— —C_2H_5 / OCH₃ H   **7**

$\uparrow h\nu$

$(CH_3)_2CO$ + H / C=C / CH₃O C_2H_5 (structure **3**)

1   **3**

Alkyl ketones possess attractive qualifications to test the simple models for ketone n,π^* states since (a) S_1 (n,π^*) and T_1 (n,π^*) of alkyl ketones are relatively "pure" because of the large $n,\pi^*-\pi,\pi^*$ splitting in these molecules[12] and (b) the relatively long-lived S_1 state of alkyl ketones (relative to aryl ketones) provides an opportunity for investigating and comparing the bimolecular photoreactions of the n,π^* singlet and triplet states of the same molecule.

The ketone-sensitized isomerization of ethylenes was originally believed to occur via a sensitizer ethylene adduct (Schenck mechanism)[13,14] but was later shown to occur at least in some cases by energy transfer from the excited sensitizer to the ground-state ethylene.[15] Recently, strong evidence for the occurrence of a Schenck mechanism for the sensitized isomerization of alkenes[16,17] has appeared. However, it has not been rigorously demonstrated that oxetane formation and cis-trans isomerization proceed via a common mechanism.

The most likely Schenck intermediate in the case of the sensitized isomerization of ethylenes by ketones is the 1,4 biradical mentioned above as a precursor to oxetanes. Thus both oxetane formation and sensitized cis-trans isomerization of ethylenes by excited ketones serve as a possible probe into the chemical nature of 1,4 biradicals, species of considerable interest for the general problem of spin correlation between free valences separated by saturated groups and because of their presumed occurrence in $2\pi + 2\pi$ dimerizations[18a] and four-membered ring decompositions.[18b]

We report here our quantitative study of the photocycloaddition of acetone to 1-methoxy-1-butene and the

acetone-sensitized cis-trans isomerization of cis- and trans-1-methoxybutene.

Results

Irradiation through Pyrex of acetone solutions of either trans-1-methoxybutene (t-MB) or cis-1-methoxybutene (c-MB) yields oxetanes **4, 5, 6**, and **7** and effects sensitized cis-trans isomerization.[19a,b]

The proof of structures **4, 5, 6**, and **7** has been published and will not be discussed here.[19b] The oxetanes **4–7** are not interconverted under our photolysis conditions.

Determination of the Excited States Involved in the Addition of Acetone to c-MB and t-MB. The ratio **4/5** and **6/7** produced by irradiation of solutions of c-MB in acetone with 3130-Å light was found to be dependent on the initial concentration of c-MB. In order to simplify quantitative measurements, **6** and **7** were conveniently eliminated from the vpc analyses by treatment of the photolysate with a few microliters of 0.01 M HCl just prior to vpc analysis. Control experiments showed that **4** and **5** were totally unaffected by the addition of HCl.[19] Figure 1 shows the dependence of **4/5** on initial concentration of c-MB. Extrapolation to zero [c-MB] leads to a value **4/5** = 1.06 ± 20%. The value of **4/5** at high [c-MB] appears to level off and approach a value of ~2.5.

These results suggest the intervention of two different excited states in the cycloaddition reaction; one state operates at low [c-MB] and results in nearly total loss of (initial olefin) stereochemistry in the oxetane formation, and the other state results in some preservation of initial olefin stereochemistry. Since it is known that acetone singlets are not measurably affected by low concentrations of piperylene (Pip)[20] while acetone triplets are quenched by Pip at a rate close to that for diffusion-controlled quenching,[20,21] we are able to test whether acetone triplets are involved in the formation of oxetanes

(12) (a) Reference 8, p 137 ff; (b) M. Kasha in "Light and Life," W. D. McElroy and B. Glass, Ed., Johns Hopkins University, Baltimore, Md., 1961, p 31; (c) H. E. Zimmerman, *Advan. Photochem.*, 1, 183 (1963).

(13) G. O. Schenck and R. Steinmetz, *Bull. Soc. Chim. Belges*, 71, 781 (1962).

(14) N. J. Turro, *Photochem. Photobiol.*, 9, 555 (1969).

(15) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Am. Chem. Soc.*, 86, 3197 (1964).

(16) N. C. Yang, J. I. Cohen, and A. Shani, *ibid.*, 90, 3264 (1968); N. C. Yang, *Photochem. Photobiol.*, 7, 767 (1968).

(17) J. Saltiel, D. R. Neuberger, and M. Wrighton, *J. Am. Chem. Soc.*, 91, 3658 (1969).

(18) (a) R. B. Woodward and R. Hoffmann, *Accounts Chem. Res.*, 1, 17 (1968); (b) H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, 72, 1866 (1968).

(19) (a) For recent work on the chemistry of 2-alkoxyoxetanes, see S. H. Schroeter, *J. Org. Chem.*, 34, 1187 (1969); (b) N. J. Turro and P. A. Wriede, *ibid.*, 34, 3562 (1969).

(20) (a) P. J. Wagner and G. S. Hammond, *J. Am. Chem. Soc.*, 87, 4009 (1965). (b) High concentrations of 1,3-pentadiene do, however, result in inefficient quenching of acetone fluorescence: S. F. Wettack, G. D. Renkes, M. G. Rockley, N. J. Turro, and J. C. Dalton, submitted for publication.

(21) R. E. Rebbert and P. Ausloos, *J. Am. Chem. Soc.*, 87, 5569 (1965).

Figure 1. The effect of c-MB concentration on 4/5.
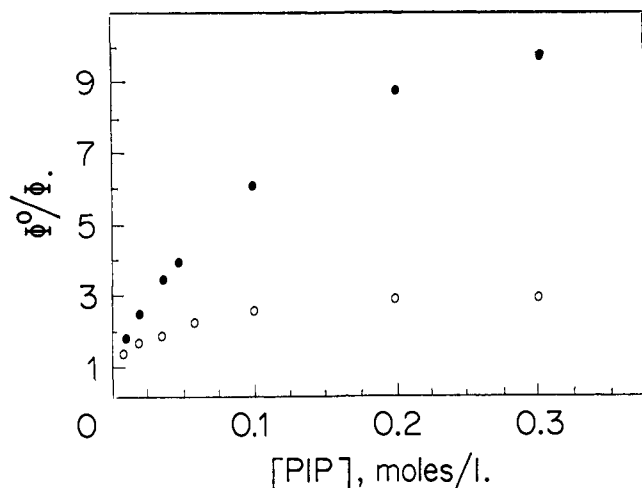

Figure 2. Quenching of acetone addition to 0.5 M c-MB by 1,3-pentadiene: O, quenching of 4; ●, quenching of 5.

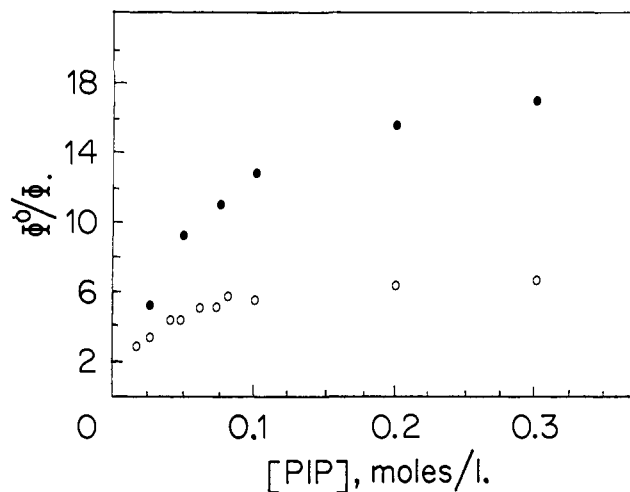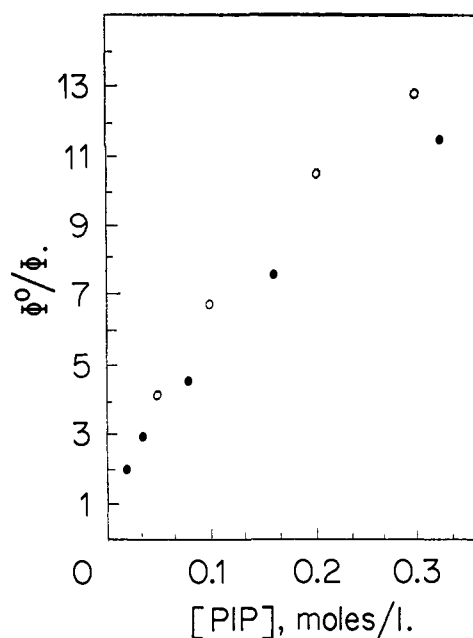Figure 3. Quenching of acetone addition to 0.5 M t-MB: O quenching of 5; ●, quenching of 4.

Figure 4. Quenching of cis–trans and trans–cis isomerization of 0.5 M MB by 1,3-pentadiene: O, trans–cis isomerization; ●, cis–trans isomerization.

simply by examining the effect of Pip on oxetane formation and by paying particular attention to the quenching of **4** and **5** as a function of [Pip]. Our results are shown in Figures 2 and 3.

The formation of both **4** and **5** is quenched by Pip, but (a) the Stern–Volmer plots of Φ^0/Φ vs. [Pip] are not linear and (b) **4** and **5** are not quenched at equal rates. Starting with c-MB the ratio **4/5** is 4.50 in the presence of 0.4 M Pip. Starting with t-MB the ratio **5/4** is 2.70 in the presence of 0.4 M Pip (Table I).

Table I. Ratio of cis- and trans-Oxetanes from MB under Different Conditions[a]

———Starting Olefin———			
t-MB 5/4	c-MB 4/5	c-MB 6/7[c]	Conditions
1.20[b]	1.35[b]	0.88[b]	Me₂CO solvent
2.70[b]	4.50[b]	2.20[b]	0.4 M 1,3-pentadiene–Me₂CO
1.04	0.97	0.65	Extrapolated to zero [MB]

[a] Accuracy of measurements ±10%. [b] Starting with 0.5 M MB. [c] Calculated by difference (see Experimental Section).

As mentioned above, cis–trans isomerization of MB competes with cycloaddition of acetone to MB. Pip quenches the cis–trans isomerization of MB (Figure 4). Because we were unable to obtain either t-MB or c-MB without ∼0.5% contamination with the other geometric isomer, at high concentrations of Pip, subtraction of initial amounts of isomerized olefin from the photoisomerized olefin introduces a large error (especially at low conversions). Nevertheless, it can be seen from Figure 4 that at high [Pip] the value of Φ^0/Φ begins to level off, suggesting that *some olefin isomerization comes from singlet sensitization.* At 0.58 M c-MB, $\Phi_{c\to t}$ was found to be 0.085 and at 0.5 M t-MB, $\Phi_{t\to c}$ was found to be 0.06 (Table II).

The leveling off of oxetane formation (Figures 2 and 3) at high [Pip] provides strong evidence that singlet addition is essentially the sole path for cycloaddition at [Pip] = 0.4 M. Thus, we are able to obtain kinetic
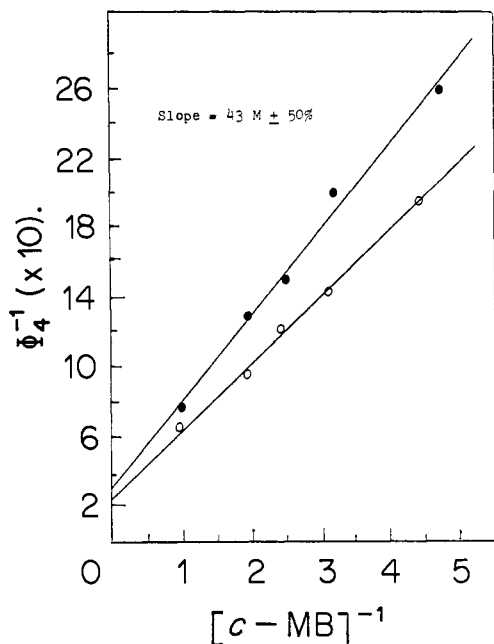
Figure 5. The effect of c-MB concentration on ϕ_4 at 0.4 M 1,3-pentadiene: ●, run no. 1; ○, run no. 2.

Figure 6. The effect of t-MB concentration on ϕ_4 and ϕ_5 at 0.4 M 1,3-pentadiene: ●, ϕ_4; ○, ϕ_5.

data on the singlet cycloaddition by plotting $1/\Phi_4$ and $1/\Phi_5$ vs. [MB] at a concentration of Pip (0.4 M) sufficient to quench all acetone triplets. These results are given in Figures 5 and 6. The Stern–Volmer plots are linear, thereby justifying the assumption that there is no significant triplet cycloaddition occurring in the presence of 0.4 M Pip. The limiting quantum yield of 4 is 0.02 from c-MB, while the limiting quantum yield of 5 from t-MB is 0.005.

Table II. Limiting Quantum Yields for Total Oxetane Formation and cis–trans Isomerization[a]

	$\Phi_{ox}{}^{c\text{-MB}}$	$\Phi_{ox}{}^{t\text{-MB}}$	$\Phi_{c \to t}{}^{c\text{-MB}}$	$\Phi_{t \to c}{}^{t\text{-MB}}$
S_1	0.04	0.01		
T_1	0.08	0.02	0.085	0.06

[a] Concentration of MB approximately 0.5 M in acetone solvent. Values for T_1 reaction are estimated from known limits for S_1 reaction and are corrected for S_1 reaction. Owing to inherent error in assumptions, the error estimate is about ±50%.

Let us now consider the kinetics of singlet quenching of acetone by MB. The simplest mechanism for singlet quenching which is consistent with all of the data available to us is

$$A_1 + t\text{-MB} \xrightarrow{k_{qt}{}^1} \text{quenching of } A_1$$

$$A_1 + c\text{-MB} \xrightarrow{k_{qc}{}^1} \text{quenching of } A_1$$

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

$$A_1 \xrightarrow{k_t} A_0 + h\nu_f$$
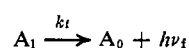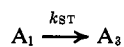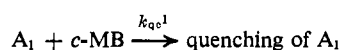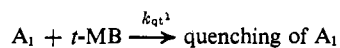
where A_1 = acetone singlet or its kinetic equivalent and A_3 = acetone triplet.

Independent studies[22] of acetone photochemistry have shown that in the absence of MB all acetone singlets

(22) R. F. Borkman and D. R. Kearns, *J. Am. Chem. Soc.*, **88**, 3467 (1966); *J. Chem. Phys.*, **44**, 945 (1966).

either intersystem cross or fluoresce and that $k_{ST} \gg k_f$. Thus, the total rate of deactivation of singlet acetone in the presence of MB will be determined by the sum $k_{qt}{}^1[t\text{-MB}] + k_{qc}{}^1[c\text{-MB}] + k_{ST}$. The following Stern–Volmer expressions are useful in analyzing our kinetic data for singlet addition

$$\frac{1}{\Phi_4} = \frac{1}{a_4} + \frac{k_{ST}}{a_4 k_{qc}{}^1[c\text{-MB}]}$$

$$\frac{1}{\Phi_5} = \frac{1}{a_5} + \frac{k_{ST}}{a_5 k_{qt}{}^1[t\text{-MB}]}$$

where a_4 and a_5 are the fraction of quenched singlet acetone molecules which go on to form 4 and 5, respectively.

From the slopes and intercept in Figures 5 and 6 and a value of 5×10^8 sec^{-1} for k_{ST}, we calculate $k_{qc}{}^1 = 3.2 \times 10^8$ M^{-1} sec^{-1} ± 50% and $k_{qt}{}^1 = 3.4 \times 10^8$ M^{-1} sec^{-1} ± 50%. In a completely independent experiment, it was found that at 2 M MB (mixture of cis and trans isomers) acetone fluorescence was quenched ∼50%. Using this result and the value for k_{ST}, $k_q{}^1$ is estimated to be equal to ∼2.5 × 10^8 M^{-1} sec^{-1}, in reasonable agreement with the values obtained from Stern–Volmer analysis.

The quenching of triplet acetone by MB and Pip requires addition of the following steps to the over-all mechanism. A Stern–Volmer equation for quenching

$$A_3 + t\text{-MB} \xrightarrow{k_{qt}{}^3} \text{quenching of } A_3$$

$$A_3 + c\text{-MB} \xrightarrow{k_{qc}{}^3} \text{quenching of } A_3$$

$$A_3 \xrightarrow{k_t} A_0$$

$$A_3 + \text{Pip} \xrightarrow{k_q} A_0 + \text{Pip}_3$$
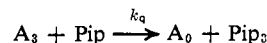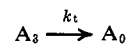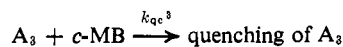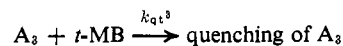
of cycloaddition to form 4 from c-MB at low conversion and in the absence of singlet addition to c-MB becomes

$$\frac{\Phi_4{}^0}{\Phi_4} = 1 + \frac{k_q[\text{Pip}]}{k_{qc}{}^3[c\text{-MB}] + k_t}$$

Turro, Wriede | 1-Methoxy-1-butene

Similarly, for the quenching of formation of **5**, starting from *t*-MB we have

$$\frac{\Phi_5{}^0}{\Phi_5} = 1 + \frac{k_q[\text{Pip}]}{k_{qt}{}^3[t\text{-MB}] + k_t}$$

One can obtain the slope of the triplet quenching plots by subtracting the amount of oxetane formed *via* the singlet state from the total yield at each quencher concentration, and then obtaining individual slopes for the remaining triplet portion of the reaction. Treatment of the data in this way leads to the results given in Table III. Thus, $k_q/(k_{qc}{}^3(0.5) + k_t)$ is 100 M^{-1}, and for

Table III. Rate Constants for Quenching of Acetone Singlets and Triplets by 1-Methoxy-1-butene

	A_1	A_3
k_{qt}	3.4×10^8 [a]	7.0×10^7 [c]
k_{qc}	3.2×10^8 [b]	1.7×10^8 [d]

[a] Starting with *t*-MB. Accuracy ±50%. [b] Starting with *c*-MB. Accuracy ±50%. [c] Starting with *t*-MB. See Results for a discussion of these values. [d] Starting with *c*-MB. See Results for a discussion of these values.

$k_q/(k_{qt}{}^3(0.5) + k_t)$ the slope is 230 M^{-1}. These values are subject to an error of about ±50%.

We can now calculate the value of rate constants $k_{qc}{}^3$ and $k_{qt}{}^3$ since k_t for quenching of A_3 by Pip in benzene is known to be equal to the diffusion control quenching constant[20] which we shall estimate to be 1×10^{10} M^{-1} sec^{-1}. Since k_t for acetone in aerated solution[23] is known to be $\sim 10^7$ sec^{-1}, we can finally estimate $k_{qc}{}^3$ $\sim 1.7 \times 10^8$ M^{-1} sec^{-1} and $k_{qt}{}^3$ $\sim 7 \times 10^7$ M^{-1}. It was of interest to determine if the selectivity ratio $(4 + 5)/(6 + 7)$, which reflects the direction of attack of excited acetone on MB, is dependent on whether singlet or triplet acetone attacks MB. A solution of 0.5 M *c*-MB in acetone was irradiated in the presence and absence of 0.4 M Pip. Analysis of these solutions revealed that $(4 + 5)/(6 + 7) = 1.23 \pm 0.05$ in the presence of Pip and that for triplet cycloaddition $(4 + 5)/(6 + 7) = 1.27 \pm 0.05$ in the absence of Pip.[24] Within relatively wide precision and accuracy limits, we feel that it is safe to conclude that the rates of quenching of both acetone singlets and triplets by MB are of the same order of magnitude.

Some preliminary studies of the ability of different sensitizers to effect *cis–trans* isomerization of the methoxybutenes are reported in Table IV. The occurrence of both oxetane formation and *cis–trans* isomerization was monitored by nmr spectroscopy.

Table IV. Effect of Various Sensitizers on *cis–trans* Isomerization of 1-Methoxy-1-butene[a]

Sensitizer	E_3[b]	T_1[c]	Cyclo-addition[d]	Isomerization[d]
Acetone	78	n,π*	Yes	Yes
Acetophenone	74	n,π*	Yes	Yes
Benzophenone	69	n,π*	Yes	Yes
Triphenylene	68	π,π*		No
2-Acetonaphthone	59	π,π*	No	No
Biacetyl	55	n,π*	Yes	Yes

[a] Benzene solution, except for the case of acetone which was employed as solvent. [b] J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, New York, N. Y., 1966, p 696. [c] N. J. Turro, "Molecular Photochemistry," W. A. Benjamin and Co., New York, N. Y., 1965, p 137 ff. [d] Analysis made by nmr which allowed ready detection of oxetanes and *cis–trans* isomerization (see Experimental Section).

Discussion

Oxetane Formation. The fact that *cis*- and *trans*-oxetanes are both formed starting with either *c*-MB or *t*-MB and acetone implies that (a) an intermediate (or intermediates) of sufficient lifetime for loss of stereochemistry is involved or (b) *cis–trans* isomerization (direct or sensitized) of the methoxybutenes occurs faster than cycloaddition. The latter possibility is rigorously ruled out by the experimental observations that (a) both *cis*- and *trans*-oxetanes are formed even under conditions of such low conversion that negligible *cis–trans* isomerization occurs and (b) the rates of addition of *c*-MB and *t*-MB to photoexcited acetone (*vide infra*) are quite similar. The questions which now arise are (a) is more than one intermediate involved, and (b) what is the chemical nature of the intermediate(s)?

The data in Table I require the intervention of at least two intermediates in the formation of **4** and **5** (at least two intermediates are required to explain our data for **6** and **7** also, but since the arguments we will make are parallel to those for formation of **4** and **5**, we shall explicitly consider only the latter pair). The following results place important constraints on any acceptable mechanisms.

(a) At 0.5 M MB oxetane formation is partially, but not completely, quenched by 1,3-pentadiene.

(b) Oxetane formation is nonstereospecific when low concentrations (<0.1 M) of MB are employed.

(c) Oxetane formation is more stereospecific at high concentration (>1 M) of MB than at low concentration (<0.1 M) of MB.
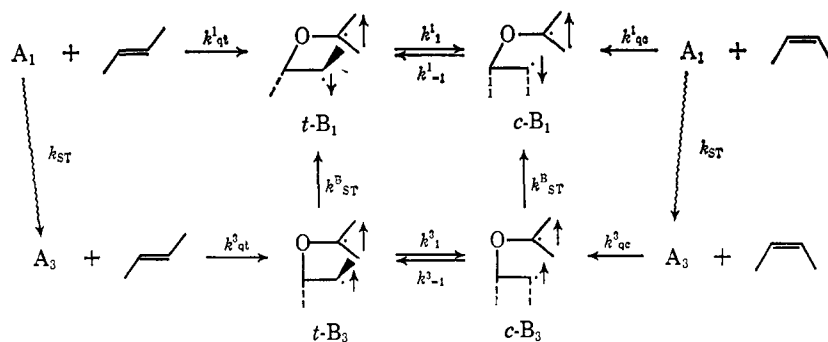
(d) At low concentration (<0.1 M) of MB in the presence of 0.4 M 1,3-pentadiene, the stereospecificity of oxetane formation is essentially that achieved by a high concentration (>1 M) of MB.

(e) The sensitized isomerization of *c*-MB → *t*-MB and *t*-MB → *c*-MB decreases in efficiency as the concentration of MB increases.

(f) The sensitized isomerization *c*-MB → *t*-MB is partially, but not completely, quenched by 0.4 M 1,3-pentadiene.

(g) MB is a relatively weak quencher of acetone fluorescence.

We propose that these data are best explained on the basis of four biradical intermediates: c-B_1 and t-B_1, biradicals formed from addition of singlet acetone to c-MB and t-MB, respectively, and c-B_3 and t-B_3, biradicals formed from addition of triplet acetone to c-

(23) Calculated if k_t for acetone = $k_q[O_2]$, with k_q = 10^{10} M^{-1} sec^{-1} and $[O_2]$ = 10^{-3} M. See also J. T. DuBois and M. Cox [*J. Chem. Phys.*, **38**, 2536 (1962)] for an experimental value which is in agreement with these assumptions.

(24) The modest selectivity of addition to C_2 relative to C_1 has been observed for other systems[25a] and contrasts with results for free-radical additions to vinyl ethers.[25b] Recently, however, the addition of propionaldehyde to ethyl vinyl ether was found to yield a *cis–trans* mixture of 2-ethoxyoxetanes as the only products in 85% yield.[25c]

(25) (a) S. H. Schroeter and C. M. Orlando, Jr., *J. Org. Chem.*, **34**, 1181 (1969); S. H. Schroeter, *Chem. Commun.*, **12** (1969); (b) E. S. Huyser and L. Kim, *J. Org. Chem.*, **33**, 94 (1968); C. Walling and E. S. Huyser, *Org. Reactions*, **13**, 91 (1963); (c) K. Shima and H. Sakurai, *Bull. Chem. Soc. Japan*, **42**, 849 (1969).

Scheme I. The Addition of A^1 and A^3 to c-MB and t-MB[a]

[a] The biradicals are shown in the cisoid conformation for convenience only. See discussion for elaboration on the conformation of B_1 and B_3.

MB and t-MB, respectively (Scheme I). The singlet biradicals can cyclize to oxetanes or cleave to re-form starting materials without violation of spin conservation rules. Thus, we anticipate that the lifetime of t-B_3 and c-B_3 may be determined by the rate at which they convert into the *lower* energy singlet biradicals.

This simple picture explains points a–g as follows. Since 1,3-pentadiene quenches acetone triplets by energy transfer at the diffusion-controlled rate,[20] but does not efficiently quench acetone singlets,[20b,21] the partial quenching of oxetane formation (point a) and *cis–trans* isomerization (point f) is consistent with attack of both acetone singlets and triplets on MB. Since the biradicals t-B_1 and c-B_1 formed by addition of singlet acetone to MB are expected to cyclize *and* fragment more efficiently relative to rotation about C–C and C–O bonds than t-B_3 and c-B_3, attack of acetone triplets on MB produces a greater loss in the stereochemistry than attack of acetone singlets on MB (point d). Since intersystem crossing from acetone singlet (A_1) to acetone triplet (A_3) competes with addition of A_1 to MB, at high concentrations of MB formation of singlet biradicals is favored over formation of triplet biradicals, thereby explaining the higher stereospecificity of oxetane formation and weak quenching of acetone fluorescence at high concentrations of MB (points c, e, and g) relative to low concentrations of MB (point b).

Having established that singlet and triplet biradicals are very probably involved in the photocycloaddition of acetone to MB, let us now consider data on the kinetics and selectivity of the cycloaddition in order to develop arguments which elaborate the nature of the transition state for biradical formation. The fact that the rate constants for quenching of A_1 and A_3 by t-MB are nearly within experimental error of each other (as well as the fact that k_{qc} for A_1 and A_3 are identical within the experimental error) is consistent with similar electronic structures for the transition state for addition of A_1 or A_3 to a given olefin isomer; that is, *the activated complex for quenching of A_1 or A_3 by MB is essentially insensitive to the spin state of the attacking excited acetone molecule*. However, bonding between the free valences of the biradical intermediates B_1 and B_3 must also be minimal or the energy of formation of the transition state leading to B_1 would be expected to be lower than that leading to B_3, since bonding of the latter is impossible (because of the parallel spin of the free valence electrons). Further evidence for the similarity of the structures of the transition states leading to B_1 and B_3 is the fact that the selectivity of attack of A_1 at C_1 of MB

(which leads to 6 and 7) relative to attack of A_1 at C_2 of MB (which leads to 4 and 5) is identical with that for attack of A_3 at these two positions (starting with c-MB)[24–26]

$$\left(\frac{4+5}{6+7}\right)_{A_1} = 1.23 \pm 0.05$$

$$\left(\frac{4+5}{6+7}\right)_{A_3} = 1.27 \pm 0.05$$

Let us now summarize the important conclusions we have made so far.

(a) Addition of A_1 and A_3 to MB proceeds *via* similar transition states which then result in formation of B_1 and B_3, respectively.

(b) At the instant of their creation, B_1 and B_3 (by Hammond's postulate)[27] should resemble the transition state leading to their formation and should also retain memory of the initial olefin geometry (*i.e.*, B_1 and B_3 are born with a *cis* or *trans* relation of the methoxy and ethyl group as shown in Scheme I).

(c) After formation of B_1, three important observable chemical events ensue: fragmentation to acetone and 1-methoxybutene, rotations about all single bonds, and closure to an oxetane (Scheme II).

(d) After formation of B_3, only two observable primary chemical events are feasible: intersystem crossing to B_1 or rotations about single bonds (Scheme I and Scheme II).

We are now in a position to consider the nature of the transition state preceding formation of B_1 and B_3 more precisely. The photoreactions of the n,π^* states of acetone are adequately described by a model which considers the n orbital on oxygen to be half-filled and electrophilic in character. Since the double bonds of t-MB and c-MB are electron rich because of donation of unpaired electrons on oxygen to the double bond, it is reasonable to expect that the reaction of A_1 or A_3 on MB will involve attack of the half-filled n orbital of the ke-

(26) The revertability of biradicals to starting materials may also play a major role in determining the observed selectivity. For example, a more stable biradical (say by formation of a C_2–O bond) may fragment more efficiently than it closes relative to a less stable biradical (say by formation of a C_1–O bond). Evidence for collapse of biradicals to starting materials has been suggested for numerous systems: (a) R. O. Loutfy, P. de Mayo, and M. F. Tchir, *J. Am. Chem. Soc.*, 91, 3984 (1969); (b) P. J. Wagner and D. J. Bucheck, *Can. J. Chem.*, 47, 713 (1969); (c) P. de Mayo, J.-P. Pete, and M. F. Tchir, *ibid.*, 46, 2535 (1968); (d) P. J. Wagner and A. E. Kempprainen, *J. Am. Chem. Soc.*, 90, 5896 (1968); (e) C. C. Bedcock, M. J. Perona, G. O. Pritchard, and B. Rickborn, *ibid.*, 91, 543 (1969), and references therein.
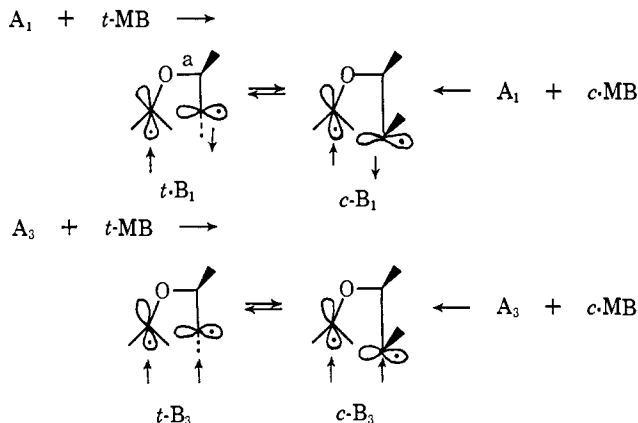
(27) G. S. Hammond, *ibid.*, 77, 334 (1955).

Scheme II. Rotational and Conformational Equilibra and Reactions of Cisoid and Transoid Biradicals[a]

tc-B   *tt*-B

cc-B   *ct*-B
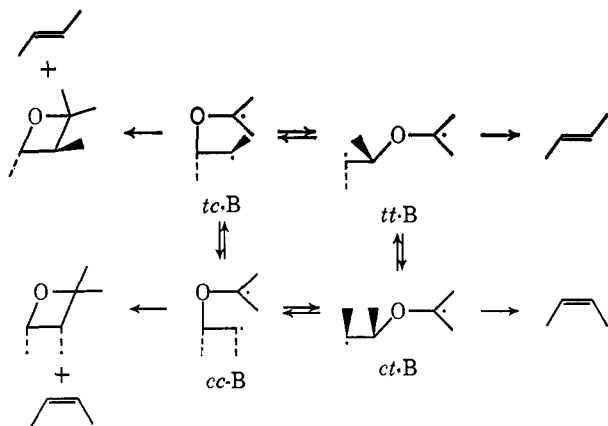
[a] Each biradical is labeled with reference to its stereochemistry about the C–C bond and the disposition of the C–C and O–C bond. The structures shown are extreme forms intended to represent the family of biradical conformers which are mainly cisoid (*i.e.*, capable of closure or fragmentation) and those which are transoid (*i.e.*, capable of fragmentation only). It should be noted that conversion of *tc*-B$_3$ to *tt*-B$_3$ may effectively be an intersystem crossing (likewise for *cc*-B$_3$ to *ct*-B$_3$).

tone n,π^* state on the π cloud of the olefin. Scheme III summarizes the possibilities. It can be seen that the

Scheme III. Attack of the ^{1}(n,π^*) and ^{3}(n,π^*) States of Acetone on *t*-MB and *c*-MB[a]

A_1 + *t*-MB $\longrightarrow$

$\rightleftarrows$ $\longleftarrow$ A_1 + *c*-MB

t-B$_1$ *c*-B$_1$

A_3 + *t*-MB $\longrightarrow$

$\rightleftarrows$ $\longleftarrow$ A_3 + *c*-MB

t-B$_3$ *c*-B$_3$

[a] The cisoid structure is shown for schematic purposes only.

expected attack of A_1 or A_3 on MB leads directly to the biradical intermediates B$_1$ and B$_3$. Probably a spectrum of orientations about bond a results from attack by excited acetone on MB. Whatever the initial orientation of the free valences relative to each other, the methoxy and ethyl groups possess the same relative orientation as the starting olefin at the instant the biradical is formed.

It is expected that the greater lifetime of a triplet biradical relative to a singlet biradical should manifest itself by a greater loss of configuration at the carbon bearing the free-radical site. In addition, since the triplet biradical is incapable of undergoing bond-making or bond-breaking processes without simultaneously violating spin conservation rules, ring closure is inhibited relative to rotations about the three single bonds separating the parallel electron centers.[28] Thus,

(28) For evidence that independent spin pairs can maintain a triplet identity over distances comparable to that expected for the transoid form B$_3$, see M. C. R. Symons, *Nature*, 213, 1226 (1967); P. W. Atkins and M. C. R. Symons, *Proc. Chem. Soc.*, 222 (1963); P. D. Bartlett and J. M.

cleavage, which *may* proceed when the biradical is in a noncisoid structure, is more likely to occur. Indeed, Bartlett and Porter[29] have provided evidence for such behavior in their study of a 1,4-hydrocarbon biradical which is produced initially specifically in the *cis* conformation *via* nitrogen extrusion from acyclic azo compound. Product distributions for thermal, direct photochemical, and sensitized photochemical formation of this biradical revealed a much higher loss of initial stereochemistry and greater fragmentation relative to ring closure in the photosensitized (triplet) reaction relative to the thermal and direct photochemical (presumably singlet) reactions. It seems likely that the triplet biradical, which is expected to be unable to cyclize or fragment during its lifetime, comes close to achieving rotational and conformational equilibrium so that the spin inversion to a singlet biradical, which must precede fragmentation or ring closure, is more likely to occur in a noncisoid conformation. Such a situation would clearly enhance fragmentation relative to closure, since the latter, but not the former, reaction *requires* a cisoid conformation as the transition state is approached.

The enhanced stereospecificity of A_1 addition could be due to either (a) greater tendency toward concerted four-center attack which competes with a relatively nonselective addition to form a truly free biradical intermediate, or (b) formation of a "free" singlet biradical which has an enhanced rate of closure relative to single bond rotation compared to the biradical formed when B$_3$ adds to MB. Two interesting aspects of the biradical which may be influencing the stereochemical results are the effect of one free valence on the other in assisting the intersystem crossing from B$_3 \rightarrow$ B$_1$ and the possibility of stabilizing association of the radical ends by dispersion interactions.[30] Bartlett and Wallbillich[31] have recently found that 1,1-dichloro-2,2-difluoroethylene adds to 1,-4-dichloro-1,3-butadiene to yield vinylcyclobutanes which show complete loss of initial diene configuration in the ring, but predominant retention of initial diene configuration in the side chain. Such behavior is best described as the result of the occurrence of a bifunctional, probably biradical, intermediate. The concomitant occurrence of a small amount of geometrical isomerization of the diene leads these authors to propose the reversible formation of a biradical intermediate, which could ring close or cleave to re-form starting materials (or isomerized diene). The rate of cleavage relative to closure (k_{-1}/k_2) was estimated to be $\sim$0.3.

$CF_2=CCl_2$

$CHCl=CH$
           $\overset{k_1}{\underset{k_{-1}}{\rightleftarrows}}$
$CH=CHCl$

$CF_2-\dot{C}Cl_2$ $CF_2\text{---}CCl_2$
$CHCl-CH$ $\overset{k_2}{\rightarrow}$ $CHCl-CH$
$CH=CHCl$ $CH=CHCl$
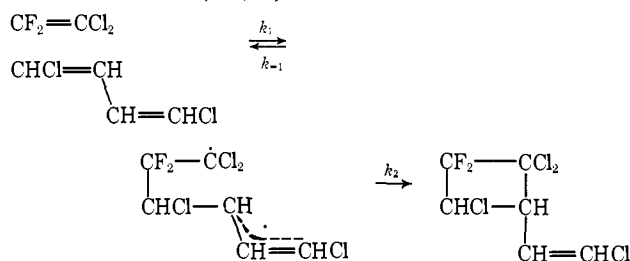
From analogous studies of the addition of 1,1-dichloro-2,2-difluoroethylene to the 2,4-hexadiene isomers, it was
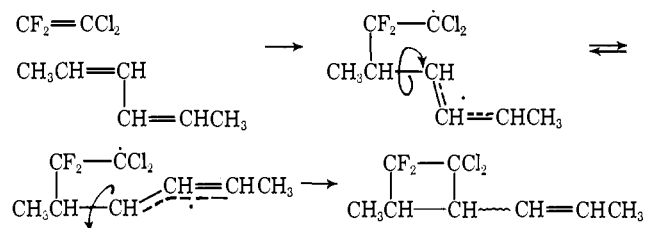
McBride, *Pure Appl. Chem.*, 15, 89 (1967); S. F. Nelsen and P. D. Bartlett, *J. Am. Chem. Soc.*, 88, 137 (1966).

(29) P. D. Bartlett and N. A. Porter, *ibid.*, 90, 5317 (1968).
(30) (a) M. Itoh and E. M. Kosower, *ibid.*, 90, 1843 (1968); (b) I. E. Morozova and M. E. Dyatkina, *Russ. Chem. Rev.*, 37, 376 (1968).
(31) P. D. Bartlett and G. E. H. Wallbillich, *J. Am. Chem. Soc.*, 91, 409 (1969).

possible to conclude that the ratio of internal rotation to ring closure[32] in the biradical was ~10.

$$CF_2=CCl_2 \qquad\qquad\qquad CF_2-\dot{C}Cl_2$$
$$CH_3CH=CH \qquad\longrightarrow\qquad CH_3CH\!\!\diagdown\!\!CH \qquad\rightleftharpoons$$
$$CH=CHCH_3 \qquad\qquad\qquad CH=CHCH_3$$

$$CF_2-\dot{C}Cl_2 \qquad\qquad\qquad CF_2-CCl_2$$
$$CH_3CH\!\!\diagup\!\!CH\!\!=\!\!CHCH_3 \;\longrightarrow\; CH_3CH\!-\!CH\!-\!CH=CHCH_3$$

The spin state of the initially formed biradical intermediate is probably singlet in these cases since there seems to be no special reason for a spin change to occur along the reaction coordinate connecting the starting materials with the intermediate.[28]

A number of answerable interesting questions concerning the biradicals B_1 and B_3 arise: (a) what are the efficiencies of formation of t-B_1, t-B_3, c-B_1, and c-B_3? (b) what is the rate of intersystem crossing from B_3 to B_1? (c) what are the relative rates of fragmentation, bond rotation, and cyclization in B_1? and (d) what is the relative rate of intersystem crossing to bond rotation in B_3? Some incomplete preliminary data relevant to point a are given in Table II. We can see that about 25% of the acetone triplets formed attack MB to form triplet biradicals which decay via oxetane formation or fragmentation. Unfortunately, the rather large error limits involved make it impossible to estimate accurately the contribution of any A_3 quenching which does result in a chemically observable consequence.[26] Points b and d above are related, in that it is possible in principle to obtain a ratio k_{ST}^B/k_{rot}, the ratio of the rate of intersystem crossing from B_3 to B_1 to the rate of bond rotation in B_3, from our data. Choosing a reasonable value for k_{rot} will then allow us to estimate k_{ST}^B. The crucial experimental parameters required to obtain k_{ST}^B/k_{rot} are the initial ratio 4/5 starting from c-MB and the initial ratio 5/4 starting from t-MB. These numbers are nearly identical within our experimental error. Analyzing our data via the method of Bartlett and Montgomery[32] and assuming the difference between the measured ratios 4/5 = 0.975 and 5/4 = 1.04 to be real, we obtain k_{ST}^B/k_{rot} ~0.01. If the rotational barriers of B_3 are of normal magnitude[33] (~3 kcal/mole), then k_{rot} ~ 5 × 10^{10} sec^{-1} so that k_{ST}^B ~ 5 × 10^8 sec^{-1}. This is an interesting result and is of considerable importance to the theory of intersystem crossing. However, the experimental error, as mentioned above, is sufficiently great that k_{ST} may be very much smaller than k_{rot}. It must be emphasized that our calculation places an upper bound on the value for k_{ST}, i.e., k_{ST} may be very much smaller than 10^8 sec^{-1}.

Mechanism of the Acetone-Sensitized *cis–trans* **Isomerization**[34] **of 1-Methoxybutenes.** Conceptually, photosensitized *cis–trans* isomerization[14] can be envisioned as occurring via (a) classical (vertical) electronic excitation transfer from the excited sensitizer to produce an electronically excited ethylene;[15] (b) nonvertical elec-

tronic excitation transfer from the excited sensitizer[35a] to produce a nonspectroscopically observable (presumably twisted) electronically excited ethylene;[35b] and (c) chemical addition of the electronically excited sensitizer to produce an unstable intermediate (of sufficient lifetime to lose the initial stereochemistry of the ethylene) which collapses to regenerate the starting ketone and ethylenes of initial and geometrically isomerized stereochemistry.[13,36]

Operationally, the occurrence of mechanism a is revealed by relative insensitivity of (1) the rate of sensitized isomerization,[37] (2) the quantum yields $\Phi_{c\rightarrow t}$ and $\Phi_{t\rightarrow c}$, and (3) the ratio of *cis* isomer/*trans* isomer at the photostationary state, to the sensitizer structure, but a predictable sensitivity of these quantities to the sensitizer energy. The occurrence of mechanism b is more difficult to predict but apparently requires a flexible acceptor ethylene which possesses a twisted electronically excited state lower in energy than that of the sensitizer (but possesses no spectroscopic electronically excited state lower than that of the excited sensitizer). This mechanism does not predict a strong effect of sensitizer structure on quantities 1, 2, and 3 listed above. Finally, for mechanism c one expects a strong dependence of quantities 1, 2, and 3 on the structure of the excited sensitizer but not necessarily a predictable sensitizer energy correlation.[17]

Yang[16] has shown that the triplet state of benzophenone (E_3 = 68.0 kcal/mole) is a common intermediate to oxetane formation and sensitized *cis–trans* isomerization of 3-methyl-2-pentene. On the basis of the failure of triphenylene (E_3 = 66.5 kcal/mole) to sensitize isomerization, it was proposed that oxetane formation and sensitized isomerization are related in the benzophenone–3-methyl-2-pentene system. It was specifically proposed that benzophenone may add to 3-methyl-2-pentene to form a (triplet)[38a] biradical intermediate (8) which may cyclize to oxetanes[38b] or dissociate to yield ground-state benzophenone and *the triplet state of the olefin in a nonplanar configuration*. Alternatively, the possibility was considered that the interaction of the n,π* benzophenone triplet might polarize the π system of the olefin such that a transition state (9) was achieved in which the olefin moiety is no longer planar and is capable of collapsing to *cis*- or *trans*-olefin. This species or transition state can also collapse to ground-state benzophenone and twisted olefin triplet. The latter mechanism is essentially an elaboration of the nonvertical excitation transfer mechanism for quenching flexible olefins proposed by Hammond and Saltiel,[35a] with the added detail that such an energy transfer will occur most efficiently (and with a high rate constant)

(32) P. D. Bartlett, *Science*, **159**, 833 (1968); L. K. Montgomery, K. Schueller, and P. D. Bartlett, *J. Am. Chem. Soc.*, **86**, 622 (1964).

(33) E. B. Wilson, Jr., *Proc. Nat. Acad. Sci. U. S.*, **43**, 816 (1957); B. Zimm and J. K. Bragg, *J. Polymer. Sci.*, **9**, 476 (1952); W. Kuhn, *Kolloid Z.*, **68**, 2 (1934).

(34) For a review of *cis–trans* isomerization, see R. B. Cundall in "Progress in Reaction Kinetics," Vol. 2, G. Porter, Ed., Pergamon Press, Oxford, 1964.

(35) (a) G. S. Hammond and J. Saltiel, *J. Am. Chem. Soc.*, **85**, 2515, 2516 (1963); (b) R. S. Mulliken and C. C. J. Roothan, *Chem. Rev.*, **41**, 219 (1947); R. McDiarmid and E. Charney, *J. Chem. Phys.*, **47**, 1517 (1967); W. J. Potts, Jr., *ibid.*, **26**, 65 (1955); L. Burnelle, *ibid.*, **43**, 529 (1965).

(36) An extreme case of chemical photosensitization is the photoinitiated iodine-catalyzed isomerization of olefins: S. W. Benson, K. W. Egger, and D. M. Golden, *J. Am. Chem. Soc.*, **87**, 3314 (1965).

(37) See W. G. Herkstroeter and G. S. Hammond [*ibid.*, **88**, 4769 (1966)] for a discussion.
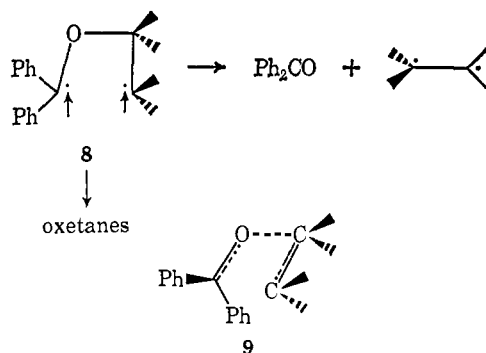
(38) (a) The spin state of the biradical intermediate is not explicitly specified in ref 16, but presumably a triplet biradical is implied; (b) again, it is not explicitly mentioned in ref 16 whether the (triplet) intermediate 8 collapses to a triplet oxetane[39] or whether spin inversion occurs to yield a singlet biradical before the ring closes.

(39) S. M. Jaspar, M. Pomerantz, and E. W. Abrahamson, *Chem. Phys. Lett.*, **2**, 137 (1968).

$$\text{Ph} \diagdown \diagup O \diagup \diagdown \quad \longrightarrow \quad Ph_2CO \; + \; \diagup \diagdown$$

8

↓

oxetanes

$$Ph \diagdown \diagup O \cdots C \diagup \diagdown$$

9

when the sensitizer is highly polarizing and the acceptor is polarizable. Saltiel[17] has shown that the acetone and acetophenone photosensitized isomerization of the 2-pentenes probably occurs *via* a Schenck mechanism. His evidence consists of the fact that a single decay ratio to *cis*- and *trans*-2-pentene is required if a common excited state of the ethylene, free of the influence of sensitizer, is formed; but, in fact, his results for sensitization by different sensitizers cannot be fit to a single decay ratio. Unfortunately, no attempts were made to relate these results to oxetane formation.

Caldwell and Sovocool[40] have interpreted data which showed a deuterium isotope effect on the photosensitized isomerization of $PhCH=C(CH_3)H(D)$ as evidence for a Franck–Condon effect on energy transfer. They feel a change in hybridization from sp^2 to sp^3 (as required by the Schenck mechanism) should show an inverse α-deuterium isotope effect, $k_H/k_D < 1$, for the sensitization step. Their data, however, show $k_H/k_D > 1$ in analogy to the deuterium effect on radiationless decay rates of triplet states of organic molecules.

Jaspar, Pomerantz, and Abrahamson[39] have proposed a "hot oxetane" intermediate to explain the formation of hexadeuteriotetramethylethylene when a solution of acetone-d_6 and tetramethylethylene-h_{12} is irradiated. There seems to be relatively little support for the generality of such a proposition. Furthermore, it does not explain the ubiquitous occurrence of *cis–trans* isomerization which almost invariably accompanies oxetane formation.[4]

Interestingly, none of these mechanisms[41] explicitly considers the attractive possibility that sensitized isomerization results from a competition between rotation about single bonds in the intermediate Schenck biradical and fragmentation of the Schenck biradical into *ground-state ketone and ethylene* (Scheme II).

There seems to be an implicit assumption that (a) the triplet ketone and ground state ethylene lead to a *triplet*[38] biradical and (b) the triplet biradical prefers to collapse to a triplet product rather than undergo spin inversion to a singlet biradical. There is no reason to believe that intersystem crossing of a triplet biradical cannot effectively compete with dissociation. Indeed, the energetics of $B_3 \rightarrow$ ketone + triplet ethylene may be sufficiently unfavorable to rule out such a mechanism unless the twisted ethylene triplet has an unexpectedly low energy content.

Our data in Table IV suggest that photosensitized isomerization of the methoxybutenes requires a sensitizer possessing a lowest n,π^* state. This result is congruent with that of Yang.[16]

Conclusion

Taken as a whole our data seem to be quite consistent with the intermediacy of two biradical radical intermediates, B_1 and B_3, which possess very similar electronic and geometric structures, but whose chemistry contrasts drastically as a result of their different spin states. The chemical processes available to B_3 appear to be confined to (a) internal rotational and conformational changes (which probably approach equilibrium) and (b) spin inversion to B_1. The latter species has process a available to it, but now two new competitive chemical processes, fragmentation and ring closure, are also available. In addition, spin inversion from $B_1 \rightarrow B_3$ is not likely because of the lower energy content of the former. As a result we expect that t-B_1 and c-B_1 will cyclize or cleave with greater retention of initial olefin stereochemistry than t-B_3 and c-B_3 in the sense that the latter pair possess greater tendency to undergo rotation and conformational equilibrium before spin inversion occurs. It should be noted that the inability of B_3 to fragment or cyclize derives from unfavorable energetics and spin conservation rules. It is conceivable that a system may be designed in which a triplet biradical can collapse to triplet products in a process which is exothermic.[42]

Experimental Section

General Procedure for Irradiations. The mechanistic studies of the acetone–1-methoxy-1-butene photoreactions, including quantum yield determinations, concentration effects, and quenching studies, were carried out on a "merry-go-round" apparatus.[43] This equipment consists of a rotating turntable having 21 holes in an inner ring and 28 holes in an outer ring surrounding a quartz immersion well. The light source was a 450-W Hanovia medium-pressure lamp having its maximum output at 3650–3663 Å with lower intensities at 3126–3132 Å. Use of the "merry-go-round" apparatus ensured that all the samples would receive the same amount of light. The Pyrex test tubes that were used were of a uniform quality; the samples to be irradiated always contained the same concentrations of ketone so that equal amounts of light were absorbed by all samples in any given run.

Samples were made up in 5- or 10-ml volumetric flasks and 1- or 2-ml portions were added to clean 10 × 75 mm Pyrex test tubes. The tubes were then corked (nondegassed) and placed in the "merry-go-round" for irradiation. In the few cases where the sample were degassed (the benzophenone photoreduction studies),[44] degassing was accomplished by subjecting the samples to a minimum of three freeze–degas–thaw cycles at pressures near 5 μ. After degassing the samples were sealed off and irradiated as described above.

In these studies, a 1-cm path of 0.002 M potassium chromate in a 1% aqueous solution of potassium carbonate was used to isolate the 3130-Å region of the medium-pressure mercury arc. With the 3130-Å filter solution present, no light was absorbed by 1-methoxy-1-butene (λ_{max} 2400 Å).

Actinometry. Uranyl oxalate was used as the actinometer for the acetone–1-methoxy-1-butene reaction. This actinometer has been described by Forbes and Leighton.[45] A stock solution of 0.42

(40) R. A. Caldwell and G. W. Sovocool, *J. Am. Chem. Soc.*, **90**, 7138 (1968).

(41) Two other possible *cis–trans* isomerization mechanisms which involve (a) orbital symmetry arguments [E. F. Ullman and N. Bauman, *ibid.*, **90**, 4158 (1968)] and (b) electronic vibrational energy transfer [S. L. Murov, R. S. Cole, and G. S. Hammond, *ibid.*, **90**, 2957 (1968)] do not appear to apply here.

(42) For example, the 2-alkylbenzophenone enol isomerization [E. F. Zwicker, L. I. Grossweiner, and N. C. Yang, *ibid.*, **85**, 2671 (1963)].

(43) F. G. Moses, R. S. H. Liu, and B. M. Monroe, *Mol. Photochem.*, **1**, 245 (1969).

(44) W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Am. Chem. Soc.*, **83**, 2789 (1961); R. P. Foss, Ph.D. Dissertation, California Institute of Technology, 1963.

(45) G. S. Forbes and W. G. Leighton, *J. Am. Chem. Soc.*, **52**, 3192 (1930).

g of uranyl sulfate and 0.45 g of oxalic acid in 100 ml of water was prepared.

This solution was irradiated for 20 min under the same conditions as the samples and was then titrated with potassium permanganate.

The titrations of both photolyzed and unphotolyzed solutions of actinometer were run as follows. A 1-ml sample of the actinometer solution was diluted with an equal volume of 10% H_2SO_4, and then heated to 60° on the steam bath. The heated solution was titrated with permanganate solution (0.034 M) until an approximate end point was reached. Subsequent samples were treated in the same way, with the exception that about 90% of the required amount of permanganate was added to the sample while cold, and the sample was allowed to stand until it became colorless. The sample was then heated to 60° and the titration continued to the end point. Three to five samples of blanks and photolyzed solutions were titrated and the average difference in the volume of permanganate needed for the blanks and the photolyzed solutions (V) was used in the calculations (eq 1); V = difference in volume of permanganate

$$I = \frac{2.5[KMnO_4]V6.023}{0.57t} \times 10^{23} \qquad (1)$$

(in liters), I = high-intensity quanta per unit time, t = time of irradiation. Intensities using this method usually ranged between 3 and 4 $\times$ 10^{16} quanta/sec. It was not observed until the uranyl oxalate actinometer had been in use for some time that the potassium chromate filter solution transmitted light at wavelengths greater than 4000 Å, a region in which the actinometer was active. Since our samples absorbed only in the 3130-Å region, the light intensity reaching the samples was less than that calculated from photolysis of the actinometer. A correction was made by running simultaneous uranyl oxalate and benzophenone-benzhydrol actinometers[44] and obtaining the ratio of light intensities measured by each. The latter actinometer did not absorb at wavelengths longer than 4000 Å. The light intensity measured by the benzophenone-

benzhydrol actinometer was found to be 0.56 that of the intensity measured by uranyl oxalate.[46] The error in determining the absolute light intensities is estimated to be about 50%.

Analyses and Quantum Yield Determinations. Solutions of acetone and olefin were routinely photolyzed to low conversions (3–10% of product, based on olefin) to minimize the extent of conversion to the other olefin isomer.

The samples were analyzed by vapor phase chromatography and concentrations of products in the 0.001–0.005 M range were easily detected. The chromatographic conditions under which the various analyses were performed varied little between runs and are outlined below.

The acetone–MB photoreactions were analyzed on a 10 ft 5% Carbowax 20M column at 100°, with a helium flow of 25 cc/min. Retention times under these conditions were 2 min for **6**, 4 min for **5** and **7**, and 5 min for **4**. The identical retention times of **5** and **7** and the tendency of **6** and **7** to decompose on the vpc column led to problems in analysis. Both **6** and **7** were quantitatively destroyed in the photolysis solution by stirring the sample with approximately 10 μl of 0.01 M HCl directly after the irradiation was stopped. In those cases where the isomerization of 1-methoxy-1-butene was studied, a 10 ft 25% $\beta\beta\beta$ column (Chrom P) at 70° was used.

Peak areas were obtained by multiplying the height of the peak times the width at half-height. This method was found to be as reliable as the use of the Disc integrator on the recorder and was in general much easier to use.

The absolute quantum yields were measured as follows. After each photolysis, 5 μl of tetrachloroethylene was added to each milliliter of solution as an internal standard. Peak areas were then obtained relative to the area of the tetrachloroethylene peak. Absolute yields were obtained by analyzing solutions containing known amounts of **4** and **5** in addition to 5 μl of tetrachloroethylene. The concentrations of **4** and **5** in the photolyzed solutions could then be calculated and the quantum yields were obtained from eq 1.

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(46) Unpublished results, David Weiss, Columbia University.

Mechanism of Permanganate Oxidation of Tertiary Hydrogen to Hydroxyl[1a]

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Abstract: The kinetics and stereochemistry of oxidation of tertiary benzylic hydrogen to hydroxyl by potassium permanganate were studied in concentrated aqueous base. The reaction is first order in both permanganate and organic compound, and it requires about 2.4 equiv of permanganate per mol of organic. At 25.0° and 2.5 M base, the second-order rate constants for γ-phenyl-, γ-phenyl-γ-d-, γ-(p-nitrophenyl)-, and γ-tolylvaleric acids are 3.8, 0.33, 1.4, and 3.5 $\times$ 10^{-3} M^{-1} sec^{-1}; 30–40% retention of configuration was observed. A mechanism which involves hydrogen atom abstraction by permanganate accommodates the experimental facts.

The oxidation of tertiary hydrogen to hydroxyl by permanganate in aqueous base is a reaction of considerable synthetic and mechanistic interest.[2] The reaction, at least in its first step, involves conversion of $>$C–H to $>$C–OH and provides a potentially useful method of chemically activating a saturated carbon. Although aspects have been investigated previously, the

mechanism of the reaction has never been clearly ascertained.

Kenyon and Symons[3] observed some time ago that certain optically active carboxylic acids, e.g., 4-methylhexanoic acid, could be oxidized to optically active lactones. These authors suggested that the reaction proceeded with carboxylate participation, and they assumed that inversion of configuration occurred at the reaction center. Subsequently, however, Eastman and Quinn[4] showed that the epimeric dihydro-α-terpineols

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(1) (a) Presented in part at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968; (b) Alfred P. Sloan Foundation Fellow.

(2) For general reviews of the field see (a) R. Stewart in "Oxidation in Organic Chemistry," Part A, K. B. Wiberg, Ed., Academic Press, New York, N. Y., 1965, Chapter I; (b) J. W. Ladbury and C. F. Cullis, *Chem. Rev.*, **58**, 403 (1958).

(3) (a) J. Kenyon and M. C. R. Symons, *J. Chem. Soc.*, 2129 (1953); (b) J. Kenyon and M. C. R. Symons, *ibid.*, 3580 (1953).