

Structural and energetic predictions for substituted **1** are summarized in Table VII. They can be extended to molecules with a topology similar to that of **1**. A prime example is propane. Analyzing $\rho(r)$, $\nabla^2\rho(r)$, and $H(r)$ of 2-propanes **13-20** (Table II) in the same way as cyclopropanes **1-12**, similar predictions with regard to CC bond length changes upon substitution of **13** can be made. Geometry optimization of **13-20** confirms these predictions (Table II), showing that π -repellers shorten and σ -repellers and π -attractors lengthen vicinal bonds. The actual effects are smaller than those observed for **1-12** which has to do with the fact that all nuclei are well shielded in the propanes with the bond paths almost coinciding with the internuclear axes. The energetic effect of the substituent on propane can be measured with the energy of the formal reaction III. The calculated values (Table



VI) show an increase in stabilizing CC,CX bond, bond interactions parallel to the increase in the electronegativity of X. For example, Li bonded with two other σ -repellers (CH₃ groups) to carbon destabilizes (enhanced interaction of C,C concentrations lumps) while F stabilizes 2-propane.

VI. Conclusion

The principle of avoidance of geminal and vicinal charge concentration provides a guideline to predict structural and energetic features of substituted cyclopropanes and molecules topologically related to cyclopropanes. Although many of the descriptive terms used in this paper may remind one of an electrostatic description of interactions between atoms, it has to be stressed that *the electron-density model developed is not an electrostatic model* since it is based on the behavior of *both the potential energy density $V(r)$ and the kinetic energy density $G(r)$*

(16) Cremer, D.; Kraka, E., to be published.

(17) HF/6-31G* geometries have been taken from the following: DeFrees, D.; Levi, B. A.; Pollack, S. K.; Hehre, W. J.; Binkley, J. S.; Pople, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 4085-4089.

as covered by the Laplacian of $\rho(r)$ (see eq 2).

Also, it is important to note that the electron density model of 3MRs does not simply rephrase the facets of the Walsh MO model. The difference between the two models becomes apparent when considering the F substituent, once as a " π -donor" and once as a " π -repeller". While in the MO picture it is reasonable to speak of a charge transfer from the lone-pair $p\pi$ orbitals of F to the Walsh MOs of the 3MR, such a charge transfer is not obvious from the density and concentration distribution calculated for either **2** or **10**. The F atom is strongly electronegative, pulling electron density toward its nucleus from all directions and concentrating it in the way revealed by $-\nabla^2\rho(r)$. There is no indication of a "recycling process" of density in a σ -acceptor/ π -donor fashion. F causes only a redistribution of charge at the neighboring atom. Observations like this have led us to refrain from classifying substituents in "donors" and "acceptors" as is usually done in MO theory.

One has also to realize that $\rho(r)$ and all its properties lead to a "static" description of the molecule, i.e., they provide a priori no answer to questions such as "what happened when the atoms came together and formed the molecule?". However, the two-step analysis of $\rho(r)$ and $\nabla^2\rho(r)$ presented above offers some insight into this problem. For example, the investigation of compounds **1-20** suggests a relatively simple pattern of atom,atom interactions, which can be used for predictive purposes. The observation that geminal and vicinal charge concentrations try to avoid each other suffices to rationalize substituent,ring interactions of cyclopropanes also in those cases where the Walsh model is difficult to apply.

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Picosecond Dynamics of the Paterno-Buchi Reaction

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Abstract: The photocycloaddition of aromatic ketones and electron-rich olefins is found to proceed through the formation of a 1,4-biradical, and the absorption spectrum of the transient is reported in the reactions of benzophenone and xanthone with 1,4-dioxene. The biradical is found to be unstable, and one mode of decay of the species is heterolysis to a contact ion pair. The mechanism for the cycloaddition is discussed in terms of direct formation of the biradical without the intermediacy of an exciplex or charge-transfer species.

The photocycloaddition reaction of an olefin to a ketone, the Paterno-Buchi reaction,^{1,2} has been the subject to numerous investigations owing to the importance of its synthetic utility. The mechanistic studies of Arnold³ on triplet-state reaction of the ketone suggested that an intermediate between the excited state and product must intervene along the reaction coordinate. This was principally based upon the demonstration that the photo-reaction of benzophenone with *cis*- or *trans*-2-butene yields es-

entially the same mixture of the *cis*- and *trans*-oxetane (1:9) regardless of the stereochemistry of the starting olefin. These results suggested the intermediacy of a 1,4-biradical species that would allow for free rotation about the terminal bond.

Despite the success of the 1,4-biradical hypothesis, there is some evidence which intimates a more complicated picture of the reaction profile. The exceptions to the most stable biradical rule and the apparent anomalous deuterium isotope effect led Caldwell⁴

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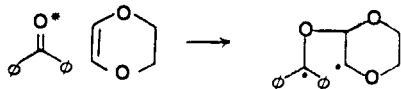
(1) Paterno, E.; Chieffi, G. *Gazz. Chim. Ital.* **1909**, *39*, 431.

(2) Buchi, G.; Inman, C. G.; Lipinsky, E. S. *J. Am. Chem. Soc.* **1954**, *76*, 4327.

(3) Arnold, D. R. *Adv. Photochem.* **1968**, *6*, 301.

to propose an intermediate intervening between the excited state and the biradical; the most likely candidate for this transient is believed to be a π -bonded complex involving charge-transfer interaction. This proposal has received further support from the studies of Wagner⁵ and Winnik.⁶

As the proposed nature of the intermediates occurring along the reaction coordinate stems largely from indirect measurements, we undertook an investigation,⁷ utilizing picosecond absorption spectroscopy, of the Paterno-Buchi reaction. When benzophenone is irradiated in the presence of 1 M dioxene in acetonitrile, the triplet state of benzophenone is quenched by dioxene in 175 ps, producing a new transient characteristic of the 1,4-biradical.



Subsequent to this initial report, further evidence for the 1,4-biradical was obtained from Caldwell's⁸ picosecond absorption studies of the photocycloaddition of benzophenone with tetramethylethylene and ethyl vinyl ether. In both studies there is no spectroscopic data supporting the formation of a charge-transfer intermediate prior to biradical formation. Therefore, we have extended our preliminary study in order to elucidate more fully the reaction mechanism for the formation of the 1,4-biradical.

Experimental Section

The picosecond absorption spectrometer has been previously described.⁹ Briefly, it consists of a mode-locked Nd³⁺-YAG (Quantel International YG-400), 10 Hz laser with pulse duration of 25 ps. A 0.5-mJ pulse is used for excitation. The continuum, 450–750 nm, is dispersed by a spectrograph (JY-200) and detected by an OMA II (PAR-1215-1216-1205I) Vidcon system.

Benzophenone (MCB), fluorenone (Aldrich), xanthone (Aldrich), and 4-phenylbenzophenone (Chemicals Procurement Laboratories) were recrystallized from ethanol. 1,4-Dioxene was fractionally distilled. Dihydropyran (Aldrich) and 2,3-dimethyl-2-butene (Aldrich) were purified by fractional distillation. 1,4-Diazabicyclo[2.2.2]octane (DABCO, Aldrich) was purified by sublimation. Spectrograde acetonitrile (Aldrich) was used. 1,2-Dimethoxyethane (DME, Aldrich) was dried by standard techniques and stored under argon and over molecular sieves. Dimethyl sulfoxide (Me₂SO, Aldrich), cyclohexane (Aldrich), dimethylformamide (Aldrich), and ethanol (U.S. Industrial Chemicals Co.) were used as received.

Results and Discussions

(A) Benzophenone/Dioxene. The choice of the appropriate olefin for this study is an important issue. The olefin must be one which undergoes reaction with the excited ketone at such a rate that subsequent processes can be detected on the picosecond time scale. If the quenching of the triplet state by the olefin is too slow, the subsequent processes will become unobservable if they take place at rates greater than the initial quenching. In addition, the olefin must not absorb a significant fraction of the excitation light lest the reaction become complicated by participation of the excited olefin molecule.¹⁰ The triplet state of the olefin must lie above that of the ketone in order to eliminate triplet-triplet energy transfer. Finally, the olefin should be one without allylic hydrogens which can be abstracted by the excited ketone.

An olefin that meets the criteria listed above is 1,4-dioxene. The photocycloaddition of 1,4-dioxene with benzophenone has been carried out previously,¹¹ forming 7,7-diphenyl-2,5,8-trioxabicyclo[4.2.0]octane with 90% yield based on recovered starting material. The olefin, a divinyl ether, has a triplet energy above that of benzophenone¹² and has no allylic hydrogen. The low ionization potential of the olefin (7.5 eV) suggests

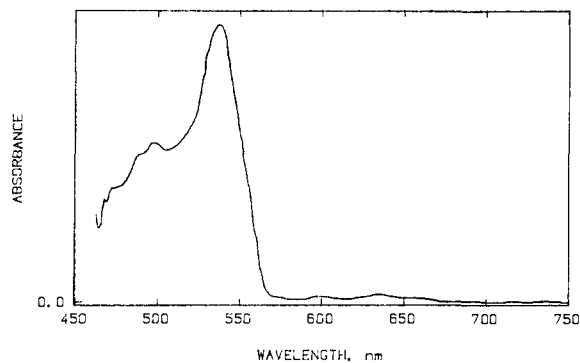


Figure 1. 1,4-Biradical formed in the irradiation of 0.05 M benzophenone-1 M dioxene in acetonitrile at 500 ps. The absorbance at 535 nm is 0.20 OD.

Table I. Solvent-Dependent Quenching of Benzophenone Triplet by 1 M Dioxene

solvent	$\tau_{1/2}$ (ps)	ϵ	$E_T(30)$
ethanol	96	25	51.9
DME	120	7	38.2
Me ₂ SO	162	46	45.0
DMF	175	38	43.8
acetonitrile	175	37	46.0
cyclohexane	216	2	31.2

that the rate of addition to benzophenone will be high.

In the absence of quenchers, the triplet state of benzophenone in acetonitrile has a half-life of greater than 1 μ s¹³ and an absorption spectrum with a λ_{max} of 525 nm,¹⁴ appearing within 25 ps following 355-nm irradiation. Upon the addition of 1 M acetonitrile solution of 1,4-dioxene, the transient triplet of benzophenone is quenched with a $\tau_{1/2}$ of 175 ± 25 ps to generate a new species with an absorption maximum at 535 nm (Figure 1). The new species has line shape and λ_{max} remarkably similar to those of the benzophenone ketyl radical derived from the photoreduction of benzophenone in the presence of amines and alcohols.⁷ Because the irradiation of benzophenone and 1,4-dioxene yields no pinacols or benzhydrols,¹¹ the appearance of the new transient is not an indication that the ketyl radical is being formed, but that there is an intermediate which has a transition virtually identical with that of the ketyl radical. Spectral properties of biradicals formed in the Norrish type II reaction of valerophenone resemble the ketyl radical of the ketone,¹⁵ suggesting that the optical transition of the biradical is localized in the aromatic $\pi-\pi^*$ transition.

In order to ascertain whether the reaction of dioxene with the triplet state of benzophenone can be extrapolated to other olefins, we also studied the irradiation of benzophenone in the presence of 4 M 2,3-dimethyl-2-butene in acetonitrile and 1 M dihydropyran in acetonitrile. As with 1,4-dioxene the triplet state decayed to yield a spectrum identified as the 1,4-biradical absorbing at 535 nm, with a half-life of formation of 760 ± 100 ps for 4 M 2,3-dimethyl-2-butene and 403 ± 80 ps for dihydropyran.

When the photolysis of benzophenone and 1,4-dioxene (1 M) is carried out in the solvents DMF, DME, cyclohexane, ethanol, and Me₂SO, similar results are obtained. A decay of the triplet state of benzophenone is evident, followed by the appearance of a new species absorbing at 535 nm, again identified as the 1,4-biradical. The spectral profile is independent of the solvent. The results of the solvent-dependence study are displayed in Table I.

The dielectric of the medium is believed to be a major factor in controlling the rate of charge-transfer processes in solution. For example, significant dielectric-dependent rate enhancements for the quenching of aromatic hydrocarbon by amines have been reported. Mataga,¹⁶ employing the Onsager model for a dipole immersed in a continuous medium, has shown that the energy of the charge-transfer complex decreases with increasing dielectric of the solvent, which is reflected in an increase in rate of formation of the charge-transfer complex. This correlation is absent in the photoreaction of benzophenone with 1,4-dioxene (Table I).

- (4) Caldwell, R. A.; Jones, S. P. *J. Am. Chem. Soc.* **1969**, *91*, 5148.
 (b) Caldwell, R. A. *J. Am. Chem. Soc.* **1970**, *92*, 1439. (c) Caldwell, R. A.; Sovocool, G. W.; Gajewski, R. P. *J. Am. Chem. Soc.* **1973**, *95*, 2549.
 (5) Kochevar, I. E.; Wagner, P. J. *J. Am. Chem. Soc.* **1972**, *94*, 3859.
 (6) Maharaj, U.; Winnik, M. A. *J. Am. Chem. Soc.* **1981**, *103*, 2328.
 (7) Freilich, S. C.; Peters, K. S. *J. Am. Chem. Soc.* **1981**, *103*, 6255.
 (8) Caldwell, R. A.; Majima, T.; Pac, C. *J. Am. Chem. Soc.* **1982**, *104*, 629.
 (9) Simon, J. D.; Peters, K. S. *J. Am. Chem. Soc.* **1983**, *105*, 4875.
 (10) Yang, N. C.; Loesch, R.; Mitchell, D. J. *J. Am. Chem. Soc.* **1967**, *89*, 5465.
 (11) Lazear, N. R.; Schauble, J. H. *J. Org. Chem.* **1974**, *39*, 2069.
 (12) Schore, N. E.; Turro, N. J. *J. Am. Chem. Soc.* **1975**, *97*, 2482.

- (13) Porter, G.; Wilkinson, F. *Trans. Faraday Soc.* **1962**, *58*, 1686.
 (14) Greene, B. I.; Hockstrasser, R. M.; Weisman, R. *J. Chem. Phys.* **1979**, *70*, 1247.
 (15) Small, J.; Scaiano, J. C. *Chem. Phys. Lett.* **1977**, *50*, 431.
 (16) Mataga, N.; Torihashi, Y.; Ezumi, K. *Theor. Chim. Acta* **1964**, *2*, 158.

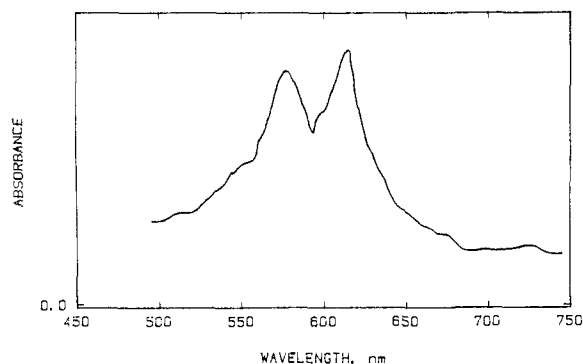


Figure 2. 1,4-Biradical formed in the irradiation of 0.05 M xanthone-3 M dioxene in acetonitrile at 100 ps. The absorbance at 609 nm is 0.10 OD.

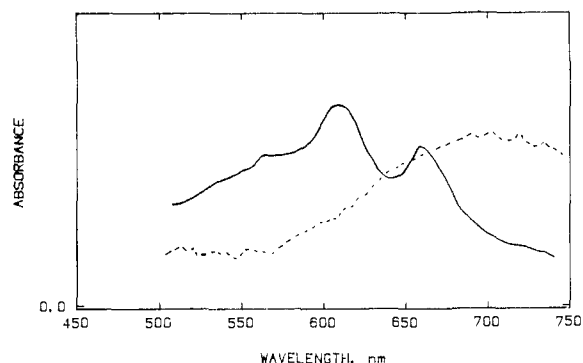


Figure 3. (—) Xanthone ketyl radical (OD 0.1) at 300 ps following irradiation of 0.05 M xanthone-1 M triethylamine in acetonitrile. (---) Xanthone radical anion (OD 0.08) at 300 ps following irradiation of 0.05 M xanthone-1 M DABCO in acetonitrile.

There is no correlation of the rate of triplet-state quenching with either the dielectric of the medium or the E_T parameter that reflects solvent polarity.

(B) Xanthone/Dioxene. Xanthone has been found to be unreactive upon photolysis with olefins.¹⁷ This lack of productive reaction has been attributed to the nature of the excited state of the ketone. It is assumed that the lowest excited state of xanthone is a triplet $\pi-\pi^*$ state, and thus should not undergo cycloaddition. Recent studies,¹⁸ however, have located a triplet $n-\pi^*$ state only 3 cm^{-1} above that of the lowest $\pi-\pi^*$ state; the separation between these two states is less than kT at room temperature, and thus one would expect significant thermal population of the $^3n-\pi^*$ state. As a result, the apparent unreactivity of xanthone in the Paterno-Buchi reaction is not a function of the nature of the excited state.

The excited-state absorption spectrum of xanthone has been reported previously¹⁴ and has an absorption maximum of 626 nm. The triplet state of xanthone has a lifetime of greater than 250 ns in acetonitrile. Upon the photolysis of xanthone (0.05 M) in an acetonitrile solution 3 M in 1,4-dioxene, the triplet state of the ketone decays with a $\tau_{1/2}$ of 27 ± 15 ps to give a new species absorbing with a dual maximum of 578 and 609 nm (Figure 2). Photolysis of xanthone (0.05 M) in the presence of 1 M triethylamine in acetonitrile yields the ketyl radical whose absorption spectrum has dual maxima at 609 and 660 nm (Figure 3). The radical anion of xanthone, produced in the irradiation of 0.05 M xanthone in an acetonitrile solution of 1 M DABCO, is formed with $\tau_{1/2}$ of 70 ± 30 ps and whose absorption spectrum has λ_{max} at 700 nm (Figure 3). On the basis of the similarity to the ketyl radical of xanthone, the species produced in the presence of dioxene is assigned to the 1,4-biradical of xanthone-dioxene.

(C) Biradical Decay. The 1,4-biradical formed in the photocycloaddition of benzophenone and 1,4-dioxene is unstable, decaying with a rate constant of $k_d = 6.3 \pm 1.0 \times 10^8\text{ s}^{-1}$ in acetonitrile. This decay may be due to a number of factors; closure to form product oxetane and β -scission are the major contributors. Because the 1,4-biradical is formed as a triplet species, intersystem crossing of the biradical must take place before any bond-forming reactions can occur. As the biradical decays, a new species appears, absorbing with a λ_{max} of 690 nm in acetonitrile

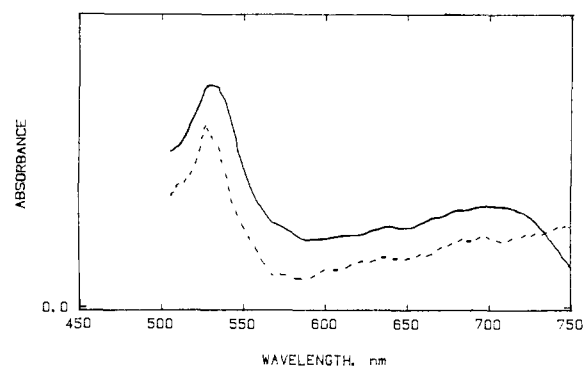
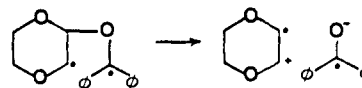


Figure 4. (---) Benzophenone/dioxene 1,4-biradical (0.1 OD, 535 nm) and benzophenone radical anion (OD 0.04, 735 nm) in Me_2SO at 1 ns. (—) In Me_2SO with 1 M NaClO_4 .

and 726 nm in Me_2SO (Figure 4). This species is identified as the radical anion of benzophenone, an assignment based upon the line shape and the λ_{max} of the well-characterized absorption spectrum of the benzophenone radical anion. The absorbance of this new transient is found to be independent of the benzophenone concentration from 0.1 to 0.4 M. This result eliminates the possibility that the radical anion is formed through a redox reaction between ground-state ketone and biradical. Thus it seems reasonable to assert that the ketone radical anion is formed through heterolysis of the 1,4-biradical to generate radical anion and an olefin radical cation:



The decay kinetics of the radical anion in Me_2SO were not monitored past 10 ns, but in that time, it was found that the radical anion concentration increased to a value approximately 20% of the excited triplet ketone concentration.

The absorption maximum of the contact ion pair formed by electron transfer from DABCO to benzophenone in acetonitrile has been found to be 690 nm, while the solvent-separated form has an absorption maximum at 715 nm.¹⁹ The absorption of the radical anion of benzophenone formed through heterolysis of the 1,4-biradical in acetonitrile is in good agreement with an assignment as a contact ion pair. In Me_2SO , the solvent-separated ion pair between benzophenone radical anion and DABCO radical cation absorbs at 735 nm, and thus the ion pair generated by β -scission of the 1,4-biradical is identified as a solvent-separated ion pair in Me_2SO . In the presence of 1 M NaClO_4 , the absorption maximum of the ion pair in Me_2SO shifts from >740 to 700 nm (Figure 4). There is no shift in the absorption maximum of the contact ion pair in acetonitrile upon the addition of 1 M NaClO_4 within 10 ns. The addition of Na^+ to the ion pair formed in Me_2SO shifts the absorption maximum to the blue, indicating a change from solvent-separated to contact ion pair with Na^+ as the counterion.²⁰ The lack of an apparent blue shift within 2 ns for the contact ion pair in acetonitrile indicates that the contact ion pair formed between the benzophenone radical anion and 1,4-dioxene radical cation in acetonitrile is not perturbed by the additional counterion on this time scale.

The biradical formed in the photolysis of xanthone and 1,4-dioxene in acetonitrile decays with a rate $k_d = 1.5 \pm 0.5 \times 10^8\text{ s}^{-1}$. No products with visible absorption spectra are observed. Similar decay kinetics are observed for the biradical in Me_2SO , but the decay of the transient is accompanied by the appearance of a new species with a λ_{max} of 700 nm. This species is similar in line shape and absorption maximum to the radical anion of xanthone in Me_2SO generated through electron transfer from DABCO to the excited triplet of the ketone (Figure 4). Thus, as in the case of the 1,4-biradical formed in the cycloaddition of benzophenone to 1,4-dioxene in polar solvents, the xanthone-derived biradical is found to undergo heterolytic cleavage to form an ion pair. It has been mentioned above that xanthone does not yield oxetanes upon photolysis in the presence of olefins; the reasons for this difference in reactivity are not apparent.

(D) Electron Transfer vs. Direct Biradical Formation. The major remaining question in the mechanism of the Paterno-Buchi reaction concerns the means of formation of the biradical: is it the result of direct attack of the excited ketone on the olefin, or is it formed after initial

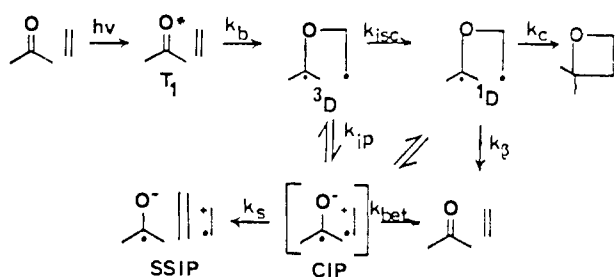
(17) Arnold, D. R.; Hinman, R. L.; Glick, A. H. *Tetrahedron Lett.* **1962**, 1425.

(18) Griesser, H. I.; Bramley, R. *Chem. Phys. Lett.* **1982**, *88*, 27.

(19) Simon, J. D.; Peters, K. S. *J. Am. Chem. Soc.* **1982**, *103*, 6403.

(20) Simon, J. D.; Peters, K. S. *J. Am. Chem. Soc.* **1983**, *105*, 4875.

Scheme I



charge transfer to generate an exciplex? As mentioned in the introduction, there is evidence which supports both views, but recent investigations have given increasing weight to the notion of the inability of the direct biradical formation mechanism to account for the data reported in the literature.

In order to investigate the question of exciplex formation prior to biradical formation, the photolysis of 4-phenylbenzophenone was studied in the presence of 1,4-dioxene in acetonitrile. Oxetane formation has been observed in the reactions of 4-phenylbenzophenone with olefins, although the yields are low.²¹ It has been shown that the $^3\pi\pi^*$ ketone undergoes electron-transfer processes with rates not very different from those found upon irradiation of benzophenone in the presence of the same donor molecules.²² However, when compared to benzophenone, the $^3\pi\pi^*$ state undergoes very inefficient hydrogen atom abstraction from 2-propanol.²³

Upon photolysis of 4-phenylbenzophenone in acetonitrile 1 M in 1,4-dioxene, no decay of the initially formed triplet state of the ketone, λ_{\max} 520 nm, is observed over 250 ns following irradiation. These results indicate that the reaction of the excited ketones with olefins forms biradicals in a mechanism involving direct attack of the ketone on the olefin. If charge-transfer intermediates are involved in the reaction mechanism prior to the formation of the diradical, it would be predicted that 4-phenylbenzophenone would undergo the reaction at rates comparable to that of benzophenone based upon the similar rates of electron-transfer reaction with DABCO.²⁰ That this correlation is not observed indicates that the Paterno-Buchi reaction may involve a polar transition state, but does not contain a local minimum characterized as a charge-transfer intermediate.

(E) Fluorenone/1,4-Dioxene. The decay process of the 1,4-biradical formed in the cycloaddition reaction may be mediated by either spin or barrier protection. If one assumes that the biradical is barrier protected, then triplet and singlet biradicals will decay with approximately equal rates. If the intermediate is spin protected, the biradical will exhibit a more rapid decay when formed from singlet excited ketones than from triplet-state reactants. We have investigated the nature of the biradical through the use of fluorenone as the excited ketone.

The lifetime of the first excited singlet state of fluorenone in polar solvents has been found to be 2.3 ns in 2-propanol.²⁴ High yields of

oxetane-derived decomposition products have been obtained upon the irradiation of acetonitrile solutions of fluorenone and olefins.²⁵ Thus the reaction of excited fluorenone with dioxene would be expected to yield a singlet biradical in a mechanism similar to that demonstrated for benzophenone.

The irradiation of 0.05 M fluorenone in the presence of a 2-propanol solution 1 M in 1,4-dioxene produces, within 25 ps, the excited singlet state with absorption maxima at 516 and 573 nm. The singlet state decays with a $\tau_{1/2}$ of 164 ± 40 ps without the appearance of a new transient. The rate of decay of the singlet state is comparable to the rate of reaction of triplet benzophenone with 1,4-dioxene, but the absence of a transient indicates that the singlet biradical undergoes closure and β -scission at a rate greater than the resolution of the experiment. Thus the triplet 1,4-biradical produced in the Paterno-Buchi reaction is spin protected. This result is consistent with the observation of stereospecific reaction with singlet ketones and olefins.

One of the compelling arguments in favor of the formation of a charge transfer species in the Paterno-Buchi reaction is the deuterium isotope studies of Caldwell.⁴ It was proposed that direct formation of a biradical would display a small inverse isotope effect as a result of the change in hybridization from sp^2 to sp^3 when using labeled olefins. A determination of the product isotope effect in the reaction of benzophenone with deuterated and protonated *cis*- and *trans*-2-butene gave a value of $k_H/k_D = 1.03 \pm 0.01$. The observation of a small direct isotope effect was found to be in conflict with the hypothesis of direct biradical formation. It was proposed that this isotope effect reflects the formation of a charge-transfer complex prior to the creation of the biradical. The fundamental assumption in these studies is that the rate of intersystem crossing of the triplet biradical is greater than the rate of formation of the biradical, contrary to observation. The results presented above demonstrate that the biradical is spin protected, and thus the rate-limiting step in the product formation is intersystem crossing.

(F) Conclusion. The mechanism for the Paterno-Buchi reaction which best accommodates all the data obtained in this work is shown in the Scheme I. Excitation of the ketone initially leads to the first excited singlet state, followed by rapid intersystem crossing to the lowest triplet state. Attack of the excited ketone on the olefin (k_b) through the electrophilic oxygen atom results in the formation of 1,4-biradical in its triplet state. Before closure (k_c) to the oxetane or β -scission (k_3) to the ground-state ketone and olefin can take place, the triplet 1,4-biradical must intersystem cross (k_{isc}) to form the singlet 1,4-biradical. The triplet biradical can, however, undergo heterolytic cleavage (k_{ip}) to form a contact ion pair prior to intersystem crossing. The ion pair may solvent separate (k_s), or intersystem cross to the singlet pair, followed by back-electron transfer (k_{bet}) to ground-state ketone and olefin or collapse to form a singlet biradical.

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Registry No. Benzophenone, 119-61-9; dioxene, 543-75-9; xanthone, 90-47-1; fluorenone, 486-25-9.

(21) Arnold, D. R. "Advances in Photochemistry"; Noyes, W., Hammond, G., Pitts, J., Eds.; Interscience: New York, 1968; p 301.

(22) Simon, J. D.; Peters, K. S. *J. Phys. Chem.* **1983**, *87*, 4855.

(23) Turro, N. J.; Lee, C. *Mol. Photochem.* **1972**, *4*, 427.

(24) (a) Kobayashi, T.; Nagakura, S. *Chem. Phys. Lett.* **1976**, *43*, 429. (b) Monroe, B. M.; Groff, R. P. *Tetrahedron Lett.* **1973**, 3995.

(25) (a) Gotthardt, H.; Steinmetz, R.; Hammond, G. S. *J. Chem. Soc., Chem. Commun.* **1967**, 480. (b) Yang, N. C. *Pure Appl. Chem.* **1964**, *9*, 591.