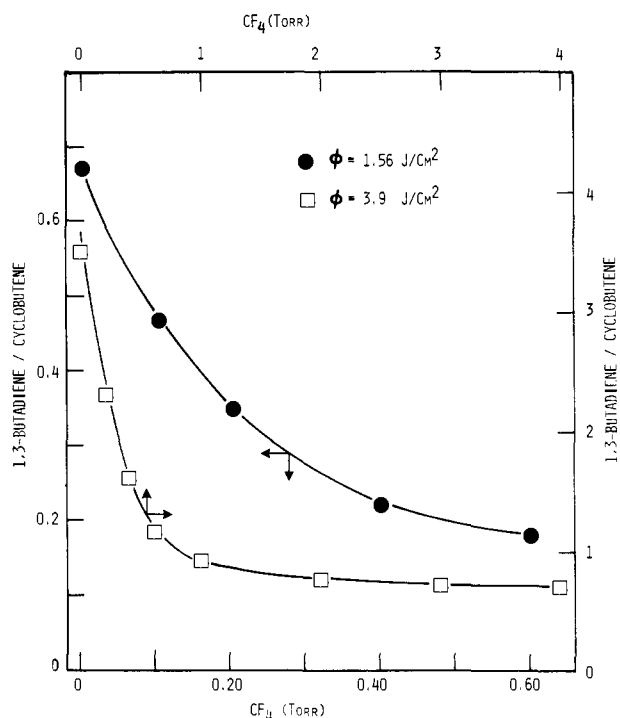**Figure 2.** Effect of CF_4 bath gas on reaction probability for 0.05-torr cyclobutyl acetate irradiated at 1078.6 cm^{-1} with ϕ = 1.56 and 3.9 J/cm^2. P_0 = reaction probability without CF_4; P = reaction probability with CF_4. Note the different scales.

Figure 3. Effect of CF_4 bath gas on the 1,3-butadiene/cyclobutene ratio for irradiation at 1078.6 cm^{-1} of 0.05-torr cyclobutyl acetate with ϕ = 1.56 and 3.9 J/cm^2. Note the different scales.

the appropriate selection of ϕ and bath gas pressure can assist in reducing the amount of secondary reaction and increasing the relative yield of the primary thermally reactive product. A lim-

(9) Nguyen, H. H.; Danen, W. C. *J. Am. Chem. Soc.*, to be submitted.

itation is imposed on the amount of bath gas added since an excessive amount will quench virtually the entire laser-induced reaction.

The synthesis of a product that is thermally more reactive than its precursor results from the ability of the pulsed infrared laser to induce high-temperature reactions but to restrict the reaction time to a few microseconds. Since this is a characteristic of infrared multiphoton processes under these experimental conditions, the effect should be general and applicable to a variety of chemical transformations.

We are continuing our investigations of the multiphoton-induced reaction of cyclobutyl acetate and will report additional aspects at a later date.

Observation of the 1,4-Biradical in the Paterno–Buchi Reaction

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Since Paterno and Chieffi first reported[1] obtaining oxetanes from the photocycloaddition of ketones to olefins in 1909, the synthetic utility of the so-called Paterno–Buchi[2] reaction has been proven. The mechanism for the reaction has come under close scrutiny for the last 20 years. The existence of a biradical in the reaction pathway has been implied by observations made by Arnold[3] of stereochemical scrambling in the product oxetanes. While a mechanism involving the direct formation of a biradical from the cycloaddition of excited ketone to olefin is appealing in its simplicity, the evidence is not inconsistent with a charge-transfer-mediated generation of the biradical.

A large body of data[4,5] supports the notion of electron transfer complexes as rapidly formed intermediates in organic photoreactions between ketones and easily oxidized reactants. Electron transfer has been invoked as a primary step in the mechanism of the Paterno–Buchi reaction in a number of recent investigations.[6,7] As a result of the short lifetimes of the putative biradical and hypothesized complexes, there has been no direct observation of these cycloaddition intermediates.[8] In this communication we report the first detection of the biradical species in the Paterno–Buchi reaction of benzophenone and dioxene (I).[8] These reactants were chosen as a result of the high yield (89%) of oxetane (II). Furthermore, no ketyl radical-derived products have been reported for this system.[9]

The experimental procedure for obtaining absorption spectra of reactive intermediates with a time resolution of 25 ps has been

(1) Paterno, E.; Chieffi, G. *Gazz. Chim. Ital.* **1909**, *39*, 341.

(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.

(4) Cohen, S. G.; Parola, A. H.; Parsons, G. H., Jr. *Chem. Rev.* **1973**, *73*, 141.

(5) (a) Wagner, P. J.; Leavitt, R. A. *J. Am. Chem. Soc.* **1973**, *95*, 3669. (b) Kochevar, I. E.; Wagner, P. J. *Ibid.* **1972**, *94*, 3859.

(6) (a) Caldwell, R. A.; Savocoal, G. W.; Gajusski, R. P. *J. Am. Chem. Soc.* **1973**, *95*, 2549. (b) Caldwell, R. A. *Ibid.* **1970**, *92*, 1439. (c) Caldwell, R. A.; Jones, S. P. *Ibid.* **1969**, *91*, 5184. (d) Caldwell, R. A.; Savocoal, G. W. *Ibid.* **1968**, *90*, 7138.

(7) (a) Schore, N. E.; Turro, N. J. *J. Am. Chem. Soc.* **1975**, *97*, 2482. (b) Turro, N. J.; Lee, C.; Schore, N. E.; Carleso, H. A. J. *Ibid.* **1971**, *93*, 3079.

(8) Hayashi, H. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2201. The author reports the observation of a transient for the Paterno–Buchi reaction of benzophenone–hexene with λ_{max} 320 nm and lifetime 25 μs, which is assigned to the 1,4-biradical. This does not agree with our observation for the 1,4-biradical.

(9) Lazear, N. R.; Schauble, J. H. *J. Org. Chem.* **1974**, *39*, 2069.
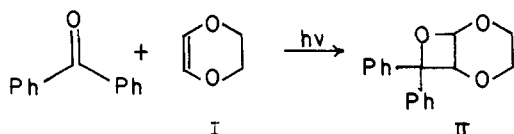
described previously.[10] In the absence of quenchers, the triplet absorption spectrum of benzophenone (λ_{max} 525 nm) (Figure 1A) is observed within 25 ps of photolysis at 355 nm and persists beyond 10 ns. In the presence of a 1 M acetonitrile solution of dioxene, the transient triplet spectrum is quenched with a half-life of $t_{1/2} = 175 \pm 25$ ps to generate a new species with an absorption maximum of 535 nm (Figure 1B). We assign this new transient as the 1,4-biradical derived from the photocycloaddition. The first optical transition of the biradical will be localized on the aromatic-centered radical. Assuming triplet radical–radical interactions to be minimal, the electronic absorption of the biradical should resemble that of the ketyl radicals.[11] Examining Figure 1 we observe similar absorption maxima and line shapes of (1) the species generated via photocycloaddition between benzophenone and dioxene and (2) the ketyl radical formed in the reaction of benzophenone with triethylamine[12a] or ethanol.[12b]

Subsequent to its formation, the biradical is found to be unstable and decays with a rate constant of $k_d = 6.3 \pm 0.9 \times 10^8$ s^{-1}. Concomitant with its decay is the appearance of a new species (Figure 1D), λ_{max} 710 nm. The observed spectrum is identical with that previously reported for the radical anion of benzophenone.[10] The time evolution of the radical anion was not monitored beyond 10 ns due to the limitations of the instrumentation. Titration experiments varying the concentration of ketone while maintaining a constant concentration of dioxene did not result in a change in the radical anion concentration. This observation rules out the possibility of radical anion formation through a bimolecular redox reaction between the biradical and ground-state ketone. The radical anion therefore must be formed via the heterolytic cleavage of the biradical into an ion pair.

Assuming the quantum yield for biradical production from triplet ketone is 1,[13] the radical anion absorption at 710 nm of 0.1 OD corresponds to an overall quantum yield for anion production from triplet benzophenone of at least 0.2. The dynamics of the formation of oxetane and regeneration of starting material were not monitored as these species fail to absorb in the visible region of the spectrum.

Although the mechanistic plausibility of the biradical in the photocycloaddition of ketones to electron-rich olefins has been recognized for many years, the nature of the biradical position on the potential energy surface for the reaction has been subject to controversy; in particular, the question of whether the radical is barrier protected has been thoroughly discussed.[14] The observed lifetime of the 1,4-biradical does not provide direct information concerning the thermal stability of the species because the biradical may also be spin protected. As benzophenone reacts with the olefin from the nπ* triplet state, the resulting biradical will be a triplet. Thus intersystem crossing must occur prior to both closure and β-scission.

To elucidate further the decay dynamics of the biradical, we examined the photocycloaddition of fluorenone and 3 M dioxene in isopropanol. In polar solvents, fluorenone does not undergo intersystem crossing on the picosecond time scale, and consequently fluorenone reacts with olefins in its lowest excited $\pi\pi$* singlet state to form a singlet biradical in these solvents. In the absence of quenchers, the first excited singlet state of fluorenone does not
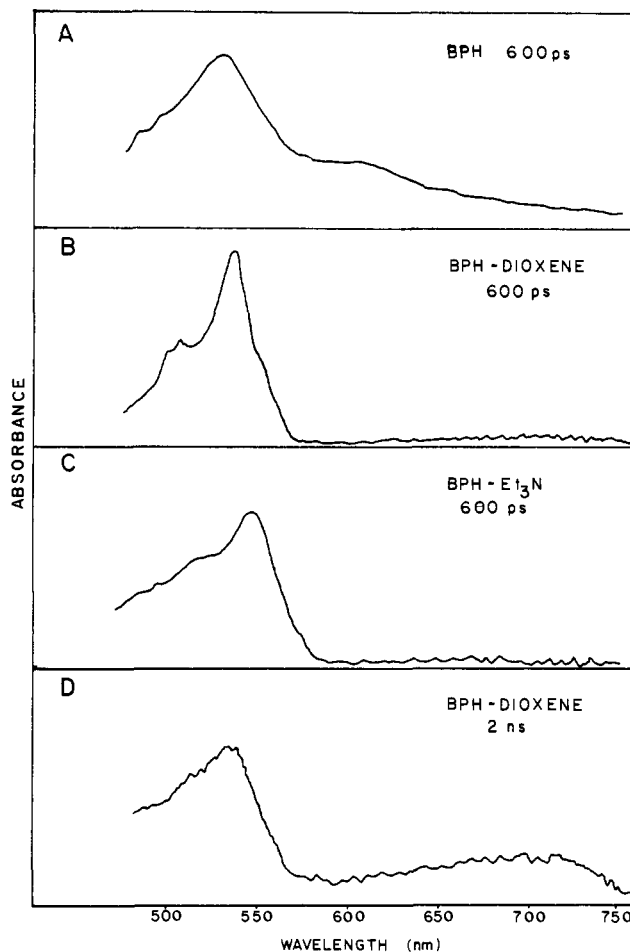
Figure 1. Transient absorption spectrum of (A) 0.2 M benzophenone in acetonitrile at 600 ps, OD = 0.50 at 525 nm; (B) 0.2 M benzophenone–1 M dioxene in acetonitrile at 600 ps, OD = 0.20 at 535 nm; (C) 0.2 M benzophenone–1 M triethylamine in acetonitrile at 600 ps, OD = 0.25 at 550 nm; (D) 0.2 M benzophenone–1 M dioxene in acetonitrile at 2 ns, OD = 0.1 at 535 nm.

decay appreciably within the first 200 ps.[10] However, in the presence of 3 M dioxene, the excited state is found to be quenched with a half-life of $t_{1/2} = 36 \pm 25$ ps. The 1,4-biradical, whose absorption spectrum will be similar to the corresponding ketyl radical of fluorenone with λ_{max} 500 nm,[15] is not observed. If the quenching of the fluorenone excited state were to proceed through a singlet biradical, then the biradical lifetime must be less than 40 ps. However, quenching of the fluorenone singlet by electron transfer followed by back-transfer to regenerate ground-state olefin and ketone cannot be ruled out at this time.

On the basis of these results and in light of previous investigations,[6,7] the following mechanism for the photocycloaddition of benzophenone to dioxene is proposed.
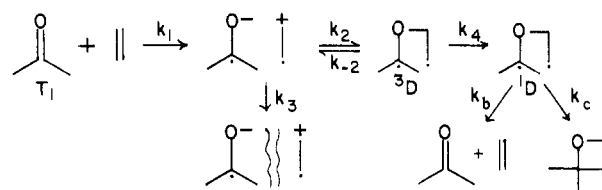
The triplet state of benzophenone is quenched by a charge transfer with rate k_1, forming a contact ion pair.[16] The contact ion pair rapidly collapses to the biradical ($k_2 \gg k_1$). As the radical anion

(10) Peters, K. S.; Freilich, S. C.; Shaefer, C. G. *J. Am. Chem. Soc.* **1980**, *102*, 5701.

(11) Small, R. D.; Scaiano, J. C. *Chem. Phys. Lett.* **1977**, *50*, 431.

(12) (a) Shaefer, C. G.; Peters, K. S.; *J. Am. Chem. Soc.* **1980**, *102*, 7566. (b) Topp, M. R. *Chem. Phys. Lett.* **1975**, *32*, 144.

(13) We have recently shown (Simon, J. D.; Peters, K. S. *J. Am. Chem. Soc.*, submitted for publication) that the radical anion and the triplet state of benzophenone have approximately equal extinction coefficients at their respective maxima.

(14) Berson, J. A. In "Rearrangements in Ground and Excited States"; deMayo, P., Ed.; Academic Press: New York, 1980; p 311.

(15) Davidson, R. S.; Santhanam, M. *J. Chem. Soc., Perkin Trans. 2* **1972**, 2355.

(16) Supporting evidence for this assignment will be presented in a future publication.

is not observed at 600 ps, it may be implied that $k_2/k_{-2} > 10$.[17] The biradical decays either by heterolytic cleavage, k_3, yielding a solvent-separated ion pair, or by intersystem crossing, k_4, followed by β-scission, k_β, and ring closure k_c, presumable with $k_c + k_\beta > k_4$. As the spin state of the ion pair is a triplet, decay to the reactants by electron transfer will not occur on the picosecond timescale.[10] With the 20% estimated yield of anion formation and the rate of decay of the biradical, $k_d = 6.3 \times 10^8$ s^{-1}, then $k_3 = 1.3 \ 10^8$ s^{-1} and $k_4 = 5.0 \times 10^8$ s^{-1}.

The lifetime of the 1,4-biradical observed in this study is shorter than that of previously studied biradicals.[11,20] The rate of decay of the biradical intermediate formed in the photocycloaddition of benzophenone and dioxene, $k_d = 6.3 \times 10^8$ s^{-1}, is substantially greater than that found[11] for the 1,4-biradical generated by Norrish Type II reaction of valerophenone, $k_d = 1.4 \times 10^7$ s^{-1}. If the lifetime of both biradicals is determined by the rate of intersystem crossing then the increase in rate by a factor of 45 may reflect that for the benzophenone–dioxene derived biradical there is (1) a larger spin–orbit coupling[18] resulting from radical interaction with oxygen and/or (2) a smaller singlet–triplet splitting resulting from greater electron delocalization over the additional phenyl substituent.[19,20] Again it is noted that the biradical derived from photocycloaddition has an alternative decay pathway, namely, heterolytic cleavage, which is independent of the biradical spin state.

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(17) Based upon the sensitivity of the instrument.

(18) Kaptein, R.; DeKanter, F. J.; Rist, G. *J. Chem. Soc., Chem. Commun.* **1981**, 499.

(19) Stephenson, L. M.; Brauman, J. I. *J. Am. Chem. Soc.* **1971**, *93*, 1968.

(20) Das, P. K.; Encinas, M. V.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 6965.

Reaction of Bicyclo[1.1.0]butanes with Pt(II) Complexes. Isolation and Characterization of New Platinacycle Compounds

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Transition-metal-catalyzed isomerization of strained cyclic hydrocarbons has been a subject of recent interest.[1] Bicyclo[1.1.0]butane (1), the smallest bicyclic hydrocarbon, and its derivatives are the molecules which have been studied most extensively. Compound 1 is rather thermally stable, but it suffers from facile rearrangements mainly into 1,3-dienes by a variety of transition-metal catalysts.[1-3] Although much effort has been directed toward the elucidation of the mechanism of catalysis,[4]

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† Research Student, Department of Chemistry, Faculty of Science, Nagoya University, April 1979–March 1981.

(1) For a review, see: (a) Paquette, L. A. *Acc. Chem. Res.* **1971**, *4*, 280–287. (b) Mango, F. D. *Coord. Chem. Rev.* **1975**, *15*, 109–205. (c) Bishop, K. C., III. *Chem. Rev.* **1976**, 461–486. (d) Halpern, J. In "Organic Syntheses via Metal Carbonyls"; Wender, I., Pino, P., Eds.; Wiley: New York, 1977; Vol. II, pp 705–730.

(2) (a) Galantay, E.; Paolella, N.; Barcza, S.; Coombs, R. V.; Weber, H. P. *J. Am. Chem. Soc.* **1970**, *92*, 5771–5773. (b) Paquette, L. A.; Zon, G. *Ibid.* **1974**, *96*, 224–233. (c) Sakai, M.; Westberg, H. H.; Yamaguchi, H.; Masamune, S. *Ibid.* **1971**, *93*, 4611–4613. (d) Gassman, P. G.; Reitz, R. R. *Ibid.* **1973**, *95*, 3057–3058. (e) Murata, I.; Nakasuji, K. *Tetrahedron Lett.* **1973**, 47–50. (f) Moriarty, R. M.; Chen, K.-N.; Flippen, J. L. *J. Am. Chem. Soc.* **1973**, *95*, 6489–6490 and references cited therein.

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Table I. Thermal Decomposition of 3

dec condition		product composition, %[a]				
solvent	temp, °C	◇⟩	◇	∿	△	△|
CH$_2$Cl$_2$	190[b]	20	18	60	0	2
	20[c]	31	40	17	12	0

[a] All products were isolated by preparative gas chromatography [GC Durapak (octane on Porasil C) treated with trimethylsilyl ester of *N*-(trimethylsilyl)ethanimidic acid, 40 °C] and identified by the comparison of mass, ^{1}H, and ^{13}C NMR spectra, and retention times of gas chromatography with those of authentic samples. [b] Pyrolysis of solid was performed under vacuum, and products were collected on a cold finger cooled with liquid N$_2$. Temperature was raised from 20 °C to the specified point at a rate of 5 °C/min. [c] The solution was stirred at 20 °C for 12 h.

numerous questions still remain to be answered: (1) how does 1 interact with the metal complexes prior to carbon–carbon bond cleavage, (2) is the intermediate a metallacyclobutane-type or a complex in which the strained C–C bond remains intact, and so on. In order to get more insight into the mechanism of the transition-metal catalyzed reactions of 1, we have studied the reactions of 1 with Pt(II) complexes. In this paper we describe the first isolation of transition-metal complexes of 1 and their unique chemical behavior.

Treatment of 1 with a catalytic amount of Zeise's dimer, [PtCl$_2$(C$_2$H$_4$)]$_2$, in acetone at 23 °C for 20 min under argon afforded butadiene in quantitative yield. When this reaction was carried out at −45 °C for 48 h, a 1:1 complex, [PtCl$_2$(C$_4$H$_6$)]$_n$ (2), was obtained as yellow-orange crystalline material in 97% yield, mp 60 °C dec. The insolubility of complex 2 in most common organic solvents made structural elucidation difficult.[5] Further treatment of a suspension of 2 in CH$_2$Cl$_2$ at −50 °C with 2 equiv of pyridine resulted in the formation of a yellow solution from which 2-[bis(pyridine)dichloroplatina]bicyclo[1.1.1]pentane (3) (Py = pyridine) was isolated as white fine crystals in 94% yield. The pure sample of 3 was obtained by column chromatography on Florisil (1:50 C$_2$H$_5$OH–CH$_2$Cl$_2$) at −60 °C in 57% yield,[6] mp 160–162 °C dec. The isolated 3 is relatively stable at room temperature, but in solution it slowly decomposes even at −25 °C.
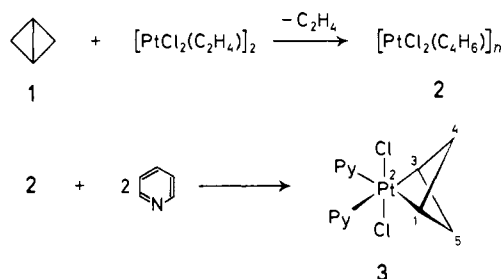
The structural assignments of 3 were done on the basis of the spectral data. Only one platinum–halogen stretching vibration was observed at 320 cm^{-1}, which is consistent with the trans-halogen structure.[7,8] The proton-decoupled ^{13}C NMR spectrum of 3 (−35 °C, ^{12}CD$_2$Cl$_2$) exhibited only two kinds of signals for the four aliphatic carbons centered at δ 19.7 (a broad signal accompanied by platinum satellites, $J_{Pt–C} = 621$ Hz, C$_1$ and C$_3$)

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(4) The intervention of allylcarbene–transition-metal complexes as the reactive intermediates have been proposed: (a) Dauben, W. G.; Kielbania, A. J., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 3669–3671. (b) Masamune, S.; Sakai, M.; Darby, N. *J. Chem. Soc., Chem. Commun.* **1972**, 471. (c) Paquette, L. A.; Wilson, S. E.; Henzel, R. P. *J. Am. Chem. Soc.* **1972**, *94*, 7771–7779. (d) Gassman, P. G.; Atkins, T. J. *Ibid.* **1972**, *94*, 7748–7756. (e) Gassman, P. G.; Reitz, R. R. *J. Organomet. Chem.* **1973**, *52*, C51–C54. For the intermolecular trapping of allylcarbene–nickel complexes with electron-dificient olefins, see ref 3.

(5) Infrared (IR) spectrum of 2 (KBr pellet): 2920 (m), 2850 (sh), 1430 (w), 1223 (s), 1090 (w), and 840 cm^{-1} (w). The thermal decomposition of 2 in vacuo at 80 °C produced the starting bicyclobutane 1 and butadiene in a ratio of 44:56.

(6) The C, H, and N analyses of 3 were satisfactory.