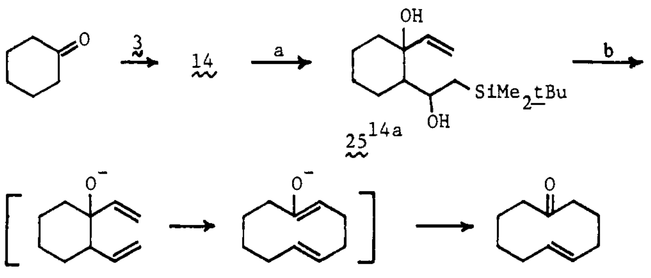
Scheme V[a]



[a] (a) $CH_2{=}CHMgCl$, THF, room temperature, 4 h. (b) KH, THF, reflux, 8 h.

tions,[18] the product β-hydroxy-*tert*-butyldimethylsilanes (6[14] and 7[14]) underwent smooth β elimination by using either the standard acidic ($BF_3\cdot Et_2O$) or basic (KH) conditions we have been using for β-hydroxy*trimethyl*silanes. Since the acid- and base-induced β-elimination reactions are known to be anti and syn respectively,[5] the addition reactions to **5** must have taken place to form predominantly the *erythro*-β-hydroxysilane **7** (in accord with Cram's rule[19,20]) in very high (up to 99%) stereselectivity.

α-*tert*-Butyldimethylsilyl aldehydes can be used to introduce vinyl groups α to the carbonyl of both ketones and esters via reaction with the lithium enolates (Scheme III). The intermediate β-hydroxysilanes were frequently unstable to distillation and were generally purified only by placing under partial vacuum to remove volatile impurities. The β-elimination reactions were carried out with $BF_3\cdot Et_2O$; attempted β-elimination reactions with KH (of **10** and **14**) led to retro-aldol reactions. The preparation of *cis*- and *trans*-ketones **21** and **17** demonstrates that substituted vinyl (alkenyl) groups can be introduced α to carbonyl; the stereoselectivity is analogous to that observed in the reactions of **5** with organometallic reagents.[26]

These reactions have also been used for the vinylation of an amino acid derivative. β,γ-Unsaturated amino acids have been of considerable recent interest because of their potent biological activity.[27] The stabase adduct **22**[28] of ethyl glycinate was converted to the β-hydroxysilane **23**[14a] in 93% yield (Scheme IV). Without purification, **23** was treated with $BF_3\cdot Et_2O$ in CH_2Cl_2 (room temperature, 16 h), effecting β elimination and deprotection of the amino group.[29] The aqueous extract was evaporated to dryness and hydrolyzed with 6 M HCl (reflux 3 h). Evaporation and cation exchange chromatography gave vinylglycine (**24**)[30] in 48% overall yield from **22**.

The use of **3** in a simple ring-growing sequence is shown in Scheme V in which KH effects both the β elimination and the anionic oxy-Cope rearrangement[31] giving cyclodecenone[32] in 49% overall yield from cyclohexanone. It should be noted that the final intermediate is an enolate anion which could, in principle, be used in another ring-growing sequence.

In summary, α-*tert*-butyldimethylsilyl aldehydes are readily prepared by hydrolysis of the corresponding imines and are versatile reagents for the stereoselective synthesis of α-vinylcarbonyl compounds. Additionally, the intermediate β-hydroxysilanes in principle could serve as latent double bonds in synthetic schemes. We are examining further applications of these reactions.

Acknowledgment. We are grateful to Professor Carlyle B. Storm and Dr. Anne Turner for 200-MHz NMR spectra of compounds **17**, **19–21** and to Dr. Anne M. Hudrlik for useful discussions and assistance with the manuscript. We thank the National Science Foundation (Grants CHE 77-10523 and CHE 79-26181) and the Dow Corning Corporation for financial support.

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(18) Some reactions which presumably involve nucleophilic attack at *t*-$BuMe_2Si$ groups have shown to be about 10^4 times slower than those at Me_3Si groups: Åkerman, E. *Acta. Chem. Scand.* **1956**, *10*, 298–305; **1957**, *11*, 373–381.

(19) Cram, D. J.; Abd Elhafez, F. A. *J. Am. Chem. Soc.* **1952**, *74*, 5828–5835. For a discussion of this and other models of asymmetric induction in nucleophilic additions to carbonyl groups, see: Nguyên, Trong Anh. *Top. Curr. Chem.* **1980**, *88*, 145–162.

(20) Surprisingly high Cram's rule stereoselectivities have been previously observed in addition reactions of α-trimethylsilyl ketones[8b,c,9b] and in the trapping of α-trimethylsilyl aldehydes (as presumed intermediates).[11,12]

(21) The isomeric purities of olefins **8** and **9** were determined as in ref 11b.

(22) Ozeki, T.; Kusaka, M. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 1995–1998.

(23) 2,4-DNP, mp 121–122 °C. Compound **13** was identical by IR and NMR spectra to a sample of **13** (2,4-DNP, mp 119.5–121 °C, satisfactory elemental analysis for C, H) prepared from the trimethylsilyl enol ether of pinacolone by addition of ethyl diazoacetate followed by reduction and treatment with acid (Hudrlik, P. F.; Bisaha, J. J., unpublished work; cf. ref 4).

(24) Crandall, J. K.; Arrington, J. P.; Hen, J. *J. Am. Chem. Soc.* **1967**, *89*, 6208–6213.

(25) With shorter reaction times, an intermediate believed to be a β-(trimethylsilyl)tetrahydrofuran was observed. On further treatment with $BF_3\cdot Et_2O$, this intermediate was converted to olefinic alcohol **19**.

(26) The stereochemistry of compounds **16–21** is based on 200-MHz NMR spectra of alcohols **19** and **20**, which showed olefinic proton coupling constants $J_{\mathrm{trans}} = 15.3$ and $J_{\mathrm{cis}} = 10.9$ Hz, respectively. Isomeric purities of olefinic ketones **17** and **21** were generally about 90–95% by VPC, depending on the particular batch of aldol **16** from which they were prepared.

(27) For recent syntheses of β,γ-unsaturated amino acids, see: (a) Friis, P.; Helboe, P.; Larsen, P. O. *Acta Chem. Scand. Ser. B* **1974**; *28*, 317–321. (b) Baldwin, J. E.; Haber, S. B.; Hoskins, C.; Kruse, L. I. *J. Org. Chem.* **1977**, *42*, 1239–1241. (c) Metcalf, B. W.; Jund, K. *Tetrahedron Lett.* **1977**, 3689–3692. (d) Greenlee, W. J.; Taub, D.; Patchett, A. A. *Ibid.* **1978**, 3999–4002. (e) Chari, R. V. J.; Wemple, J. *Ibid.* **1979**, 111–114. (f) Nunami, K.; Suzuki, M.; Yoneda, N. *J. Chem. Soc., Perkin Trans. 1* **1979**, 2224–2229. (g) Afzali-Ardakani, A.; Rapoport, H. *J. Org. Chem.* **1980**, *45*, 4817–4820. See also ref 2b and references cited therein.

(28) Djuric, S.; Venit, J.; Magnus, P. *Tetrahedron Lett.* **1981**, *22*, 1787–1790.

(29) With shorter reaction times, only N-deprotection occurred.

(30) IR and NMR spectra of **24** were in excellent agreement with reported values (ref 27a,b); recrystallization from water–ethanol gave a sample with mp 215–218 °C dec (lit.[27b] mp 218–220 °C dec).

(31) Evans, D. A.; Nelson, J. V. *J. Am. Chem. Soc.* **1980**, *102*, 774–782.

(32) Semicarbazone, mp 181–182 °C; lit. mp 178.5–179 °C. Marvell, E. N.; Whalley, W., *Tetrahedron Lett.* **1970**, 509–512.

Pulsed Infrared Laser-Induced Reaction of Cyclobutyl Acetate. Laser Synthesis of a Thermally Labile Compound by a Rapid Heating–Quenching Process

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We report the laser synthesis of an organic compound which is thermally reactive when compared to its precursor, illustrating an unique application of pulsed infrared laser radiation that cannot be accomplished by conventional thermal techniques. During the past few years, many different types of compounds have been shown to undergo infrared multiphoton absorption to produce highly vibrationally excited ground electronic state molecules. The ability of the infrared laser to excite a molecule to high effective vibrational temperatures in $\sim 10^{-7}$ s has allowed unique transformations to be effected, including selective reaction of a single component in a mixture, control of chemical equilibria, reaction of a bifunctional reactant by the normally inaccessible higher energy pathway, and generation of high concentrations of transient intermediates.[1]

The experimental methods are similar to those described elsewhere.[2,3] Upon irradiation at 1078.6 cm^{-1} (R(20) of 9-μm

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(1) For recent reviews, see: (a) Danen, W. C.; Jang, J. C. "Laser-Induced Chemical Processes"; Steinfeld, J. I., Ed.; Plenum: New York, 1981; Vol. 1, Chapter 2. (b) Danen, W. C. *Opt. Eng.* **1980**, *19*, 21. (c) Schulz, P. A.; Sudbø. Aa. S.; Krajnovich, D. J.; Kwok, H. S.; Shen, Y. R.; Lee, Y. T. *Annu. Rev. Phys. Chem.* **1979**, *30*, 379. (d) Grunwald, E.; Dever, D. F.; Keehn, P. M. "Megawatt Infrared Laser Chemistry"; Wiley: New York, 1978. (e) Bloembergen, N.; Yablonovitch, E. *Phys. Today* **1978**, *31*, 23.

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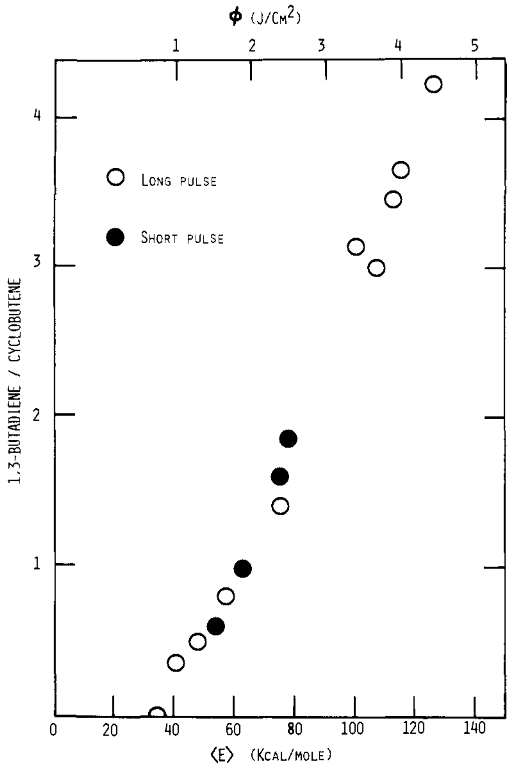
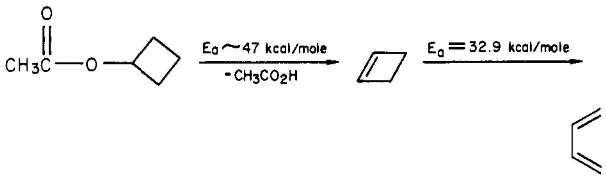


Figure 1. 1,3-Butadiene/cyclobutene ratio for irradiation at 1078.6 cm^{-1} of 0.05-torr cyclobutyl acetate vs. average absorbed energy, $\langle E \rangle$, and laser fluence, ϕ. Long pulse: 8:2:0.8 $He-CO_2-N_2$ gas mixture; initial spike ~100-ns FWHM spike + ~1.3-μs tail. Short pulse: 10:5:0 $He-CO_2-N_2$ gas mixture; ~100-ns FWHM spike, no tail.

band) 0.050 torr of cyclobutyl acetate reacts via the usual elimination process with an $E_a \sim 47$ kcal/mol to produce acetic acid and cyclobutene as the major products (reaction 1).[4] With



(1)

conventional heating, cyclobutene could never be isolated from this reaction since it undergoes a Woodward–Hoffmann-allowed conrotatory ring opening to form 1,3-butadiene with an activation energy of only 32.9 kcal/mol.[5] The cyclobutene reaction rate at 500 and 1000 K would be $\sim 9 \times 10^6$ and $\sim 8 \times 10^3$ times faster, respectively, than its rate of formation from cyclobutyl acetate.

Figure 1 depicts the 1,3-butadiene/cyclobutene ratio vs. laser fluence, ϕ, and average absorbed energy, $\langle E \rangle$; the latter was determined from the experimentally measured absorption cross section and includes the thermal energy at room temperature. It is seen that only cyclobutene is produced at $\phi = 0.8$ J/cm² but the ratio increases to >4 at $\phi = 4.4$ J/cm². The total reaction probability (cyclobutene + 1,3-butadiene) per pulse increases from 1.2×10^{-3} to 0.35 in this fluence range.

The capability of the pulsed infrared laser to generate a thermally labile product from a relatively stable precursor resides in its ability to "instantly heat" ($\sim 10^{-7}$ s) the precursor molecule to a high vibrational energy of the ground electronic state inducing nonequilibrium chemical reaction. After a few microseconds, a cooling wave intermixes the excited and surrounding cold molecules and quenches the chemical reaction in the irradiated volume, stopping the cyclobutene decomposition reaction. Although the quenching process is undoubtedly a complex interplay of bulk and molecular effects, we have estimated from reaction probability/energy absorption experiments[2] and computer modeling studies[3] that an effective reaction time of ~5–10 μs is plausible for the presently described experimental conditions. Other workers[6] have reported a similar effective reaction time although it is likely that the cooling process is quite dependent on experimental variables such as system pressure and absorbed energy.

The present observations may be explained qualitatively as follows.[7] Irradiation of cyclobutyl acetate with, e.g., 1.0 J/cm² results in an average excitation of 41 kcal/mol (43.5 kcal/mol including thermal energy at 300 K) if all the ester molecules within the irradiated volume absorb the laser radiation. Assuming that a Boltzmann distribution of vibrationally excited molecules is produced,[8] it can be calculated by RRKM theory that only ~0.9% of the excited molecules will possess sufficient energy to react in $\leq 1 \times 10^{-5}$ s or, equivalently, possess a lifetime ≤10 μs. This fraction correlates well with the experimentally observed yield per pulse of 1.5% at $\phi = 1.0$ J/cm². Note that the average energy of the *reacting* molecules, i.e., those with lifetimes ≤10 μs, is ~80 kcal/mol. Since the formation of cyclobutene and acetic acid is endothermic by 12.7 kcal/mol, the cyclobutene that is formed in the reaction process possesses an internal excitation energy of ~37 kcal/mol assuming that the energy partitions statistically between the products. It can be calculated by RRKM theory that, with this amount of vibrational excitation, only ~40% of these molecules have sufficient energy to undergo ring opening to 1,3-butadiene in <10 μs. This agrees closely with the 1,3-butadiene/cyclobutene ratio at $\langle E \rangle = 43.5$ kcal/mol in Figure 1. At higher ϕ, cyclobutyl acetate absorbs more energy, and the cyclobutene initially produced possesses higher excitation allowing more ring-opening reaction to occur before the cooling wave quenches the postpulse reaction. This is in accord with Figure 1 which depicts an enhanced 1,3-butadiene/cyclobutene ratio at high ϕ.

The 1,3-butadiene/cyclobutene ratio increases sharply with increasing cyclobutyl acetate pressure, and the amount of cyclobutene formed becomes negligible at pressures > 2 torr. The decrease in the cyclobutene yield can be ascribed to an enhanced secondary thermal reaction at high pressures. The invariance of the reaction yield at pressures > 2 torr suggests that the postpulse reaction from a thermally equilibrated system dominates over nonequilibrium laser-induced reaction under these conditions.

Figure 2 depicts the quenching effect of CF_4 bath gas on the overall reaction probability at $\phi = 1.56$ and 3.9 J/cm² corresponding to an average absorbed energy $\langle E \rangle = 54$ and 114 kcal/mol, respectively. Figure 3 shows the effect of CF_4 on the 1,3-butadiene/cyclobutene ratio at the two fluences; note the different scales. The decrease in reaction probability with increasing CF_4 is similar to that observed in other studies[2] and results from collisional quenching by CF_4. At $\phi = 1.56$ J/cm² the 90-fold decrease in total yield at 0.60 torr of CF_4 corresponds to a 60-fold decrease in the yield of cyclobutene as compared to that of the neat sample. In contrast, the absolute yield of cyclobutene at $\phi = 3.90$ J/cm² does not vary significantly with CF_4 pressure in the range 0–1.0 torr, reflecting a balance between collisional quenching of cyclobutyl acetate and cyclobutene. However, the 1,3-butadiene/cyclobutene ratio falls considerably, indicating that CF_4 is more effective at higher pressures in stabilizing the vibrationally excited cyclobutene and interdicting the consecutive ring opening to 1,3-butadiene. The large effect of bath gas on a *consecutive* reaction of a multiphoton laser-induced process contrasts with the minimal effect observed on the ratio of *competitive* reaction channels in a bifunctional reactant.[9] The significant point is that

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(3) Jang, J. C.; Setser, D. W.; Danen, W. C. *J. Am. Chem. Soc.*, submitted for publication.

(4) Some ethylene is also detected arising from the competitive relatively high energy [2 + 2] cycloreversion or biradical cleavage of the cyclobutyl ring in cyclobutyl acetate.

(5) Benson, S. W.; O'Neal, H. E. *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.* **1970**, *NSRDS-NBS 21*, 285.

(6) Steel, C.; Starov, V.; Leo, R.; John, P.; Harrison, R. G. *Chem. Phys. Lett.* **1979**, *62*, 121.

(7) A more detailed discussion will be presented in the full publication of this work.

(8) Evidence for frequency-dependent initial non-Boltzmann vibrational energy distributions in ethyl acetate and ethyl fluoroacetate has been obtained.[2,3]

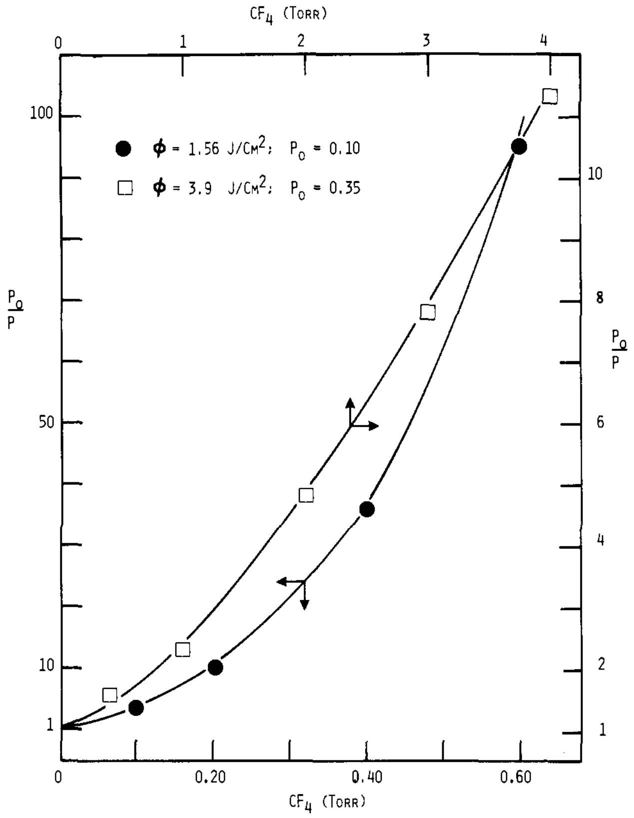

Figure 2. Effect of CF_4 bath gas on reaction probability for 0.05-torr cyclobutyl acetate irradiated at 1078.6 cm^{-1} with ϕ = 1.56 and 3.9 J/cm^2. P_0 = reaction probability without CF_4; P = reaction probability with CF_4. Note the different scales.

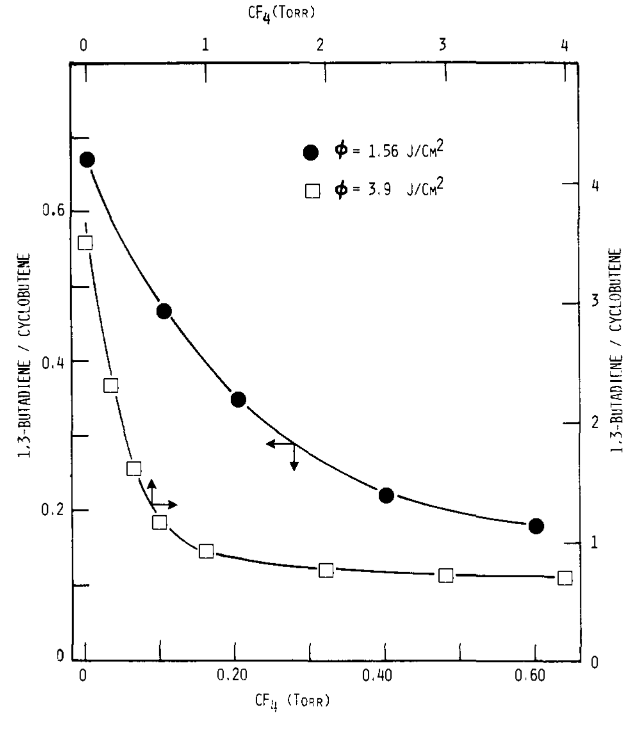

Figure 3. Effect of CF_4 bath gas on the 1,3-butadiene/cyclobutene ratio for irradiation at 1078.6 cm^{-1} of 0.05-torr cyclobutyl acetate with ϕ = 1.56 and 3.9 J/cm^2. Note the different scales.

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 limitation 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.

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

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

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

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(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.

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