

^a (a) CH₂=CHMgCl, THF, room temperature, 4 h. (b) KH, THF, reflux, 8 h.

tions,¹⁸ the product β -hydroxy-*tert*-butyldimethylsilanes (6¹⁴ and 7¹⁴) underwent smooth β elimination by using either the standard acidic (BF3.Et2O) 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, the addition reactions to 5 must have taken place to form predominantly the *erythro-\beta*-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 BF₃·Et₂O; attempted β -elimination reactions with KH (of 10 and 14) led to retro-aldol reactions. The preparation of cisand 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 22²⁸ of ethyl glycinate was con-

(18) Some reactions which presumably involve nucleophilic attack at *t*-BuMe₂Si groups have shown to be about 10⁴ times slower than those at Me₃Si groups: Akerman, 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 investmental difference of the state 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)letrahydrofuran was observed. On further treatment with BF_3 ·Et₂O, 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 $J_{trans} = 15.3$ and $J_{cis} = 10.9$ 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. r., netoc, r., Larsen, F. O. Acta Chem. Scana. Ser. B 1974; 20, 317-521.
(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. also ref 2b and references cited therein.

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

verted to the β -hydroxysilane 23^{14a} in 93% yield (Scheme IV). Without purification, 23 was treated with BF3. Et2O in CH2Cl2 (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 rearrangement³¹ giving cyclodecenone³² 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.

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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.

The experimental methods are similar to those described elsewhere.^{2,3} Upon irradiation at 1078.6 cm⁻¹ (R(20) of $9-\mu m$

⁽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.²⁷⁰ 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.

⁽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.; Sudbz. 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. (2) Danen, W. C.; Rio, V. C.; Setser, D. W. J. Am. Chem. Soc., submitted for publication

for publication.



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–CO₂–N₂ gas mixture; initial spike ~100-ns FWHM spike + ~1.3- μ s tail. Short pulse: 10:5:0 He–CO₂–N₂ gas mixture; ~100-ns FWHM spike, no tail.

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



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 $\phi = 0.8 \text{ J/cm}^2$ but the ratio increases to >4 at $\phi = 4.4 \text{ J/cm}^2$. 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 mole-

cules 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 experiments² and computer modeling studies³ that an effective reaction time of $\sim 5-10 \ \mu s$ is plausible for the presently described experimental conditions. Other workers⁶ 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 $\sim 0.9\%$ of the excited molecules will possess sufficient energy to react in $\leq 1 \times 10^{-5}$ s or, equivalently, possess a lifetime $\leq 10 \ \mu$ s. This fraction correlates well with the experimentally observed yield per pulse of 1.5% at $\phi = 1.0 \text{ J/cm}^2$. Note that the average energy of the *reacting* molecules, i.e., those with lifetimes $\leq 10 \ \mu s$, 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 $\sim 40\%$ of these molecules have sufficient energy to undergo ring opening to 1,3-butadiene in <10 μ s. 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 CF₄ 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 studies² and results from collisional quenching by CF₄. At $\phi = 1.56 \text{ J/cm}^2$ the 90-fold decrease in total yield at 0.60 torr of CF₄ 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 ϕ = 3.90 J/cm^2 does not vary significantly with CF₄ 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 CF4 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

⁽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 $\phi = 1.56$ and 3.9 J/cm². P_0 = reaction probability without CF₄; P = reaction probability with CF₄. Note the different scales.



Figure 3. Effect of CF₄ 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 lim6255

excessive amount will quench virtually the entire laser-induced reaction. The synthesis of a product that is thermally more reactive than

itation is imposed on the amount of bath gas added since an

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

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Since Paterno and Chieffi first reported¹ obtaining oxetanes from the photocycloaddition of ketones to olefins in 1909, the synthetic utility of the so-called Paterno-Buchi² 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 Arnold³ 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 chargetransfer-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

- Paterno, E.; Chieffi, G. Gazz. Chim. Ital. 1909, 39, 341.
 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 μ s, 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.

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