ever, halogen substituents do not enter into the reaction because of the high reactivity of the diazonium group. Thus, ArN_2X can be utilized as excellent precursors for the chemoselective preparation of arylpalladium species bearing a halogen group.

Experimental Section

Materials. Acetonitrile was distilled from phosphorus pentoxide (twice) and calcium hydride under nitrogen. Liquid arylamines were distilled before use under nitrogen. Guaranteed reagents of crystalline arylamines were used as received. Arenediazonium tetrafluoroborates,[15] hexafluorophosphates,[16] and chloride[17] were prepared by the ordinary methods and stored under nitrogen at −20 °C. Palladium acetate,[18] palladium trifluoroacetate,[18] bis(triphenylphosphine)palladium acetate,[18] and bis(dibenzylideneacetone)palladium[19] were prepared by the published method. Tetramethyltin and Et_4Sn were prepared by the reactions of $SnCl_4$ with MeMgBr in dibutyl ether and EtMgBr in diethyl ether, respectively. Phenyltributyltin and $CH_2{=}CHSnBu_3$ were prepared by the reactions of Bu_3SnCl with PhMgBr and $CH_2{=}CHMgBr$, respectively. Tetraphenyltin and Bu_3SnCl were used as received.

General Procedure. To a solution of an ArN_2X (0.5 mmol), a tin compound (0.6 mmol), and 2 mL of CH_3CN was added 0.05 mmol of a palladium catalyst at room temperature. After 2 h (for Me_4Sn, or 5 min for $CH_2{=}CHSnBu_3$) of stirring, an appropriate internal standard (from decane to octadecane) and 2 mL of chloroform were added to the solution. The reaction mixture was directly analyzed by GLC (silicone SE-30). The structures of all products were confirmed by comparison of the retention times on GLC with those of authentic samples (commercial origin). Some toluene derivatives were isolated by using 10 mmol of an ArN_2X, 12 mmol of Me_4Sn, 1 mmol of $Pd(OAc)_2$, and 50 mL of CH_3CN (entries 19, 21, and 23). The structure of the isolated products was confirmed by the comparison of their IR and NMR spectra with those of authentic samples.

Time Course of the Methylation. The reactions were started by addition of 2 mL of CH_3CN to a mixture of 0.5 mmol of $4\text{-}BrC_6H_4N_2BF_4$, 0.6 mmol of Me_4Sn, 0.05 mmol of a palladium catalyst, and dodecane (internal standard) in a 5-mL thermostated cell (25.4 °C) equipped with a side arm and a serum cap. Gas evolution was measured by a gas buret connected to the side arm. Samples were withdrawn at appropriate time intervals by a microsyringe and directly analyzed by GLC (silicone SE-30).

Registry No. $4\text{-}BrC_6H_4N_2^+Cl^-$, 2028-85-5; $4\text{-}BrC_6H_4N_2^+BF_4^-$, 673-40-5; $4\text{-}BrC_6H_4N_2^+PF_6^-$, 20566-57-8; $PhN_2^+BF_4^-$, 369-57-3; $2\text{-}MeC_6H_4N_2^+BF_4^-$, 2093-46-1; $3\text{-}MeC_6H_4N_2^+BF_4^-$, 1422-76-0; $4\text{-}MeC_6H_4N_2^+BF_4^-$, 459-44-9; $2\text{-}ClC_6H_4N_2^+BF_4^-$, 1956-97-4; $3\text{-}ClC_6H_4N_2^+BF_4^-$, 456-39-3; $4\text{-}ClC_6H_4N_2^+BF_4^-$, 673-41-6; $2\text{-}NO_2C_6H_4N_2^+PF_6^-$, 836-70-4; $3\text{-}NO_2C_6H_4N_2^+PF_6^-$, 1514-51-8; $4\text{-}NO_2C_6H_4N_2^+PF_6^-$, 1514-52-9; $4\text{-}NO_2C_6H_4N_2^+BF_4^-$, 456-27-9; $4\text{-}BrC_6H_4Me$, 106-38-7; PhMe, 108-88-3; $3\text{-}MeC_6H_4Me$, 108-38-3; $4\text{-}MeC_6H_4Me$, 106-42-3; $2\text{-}ClC_6H_4Me$, 95-49-8; $3\text{-}ClC_6H_4Me$, 108-41-8; $4\text{-}ClC_6H_4Me$, 106-43-4; $2\text{-}NO_2C_6H_4Me$, 88-72-2; $3\text{-}NO_2C_6H_4Me$, 99-08-1; $4\text{-}NO_2C_6H_4Me$, 99-99-0; $PhCH{=}CH_2$, 100-42-5; $4\text{-}MeC_6H_4Ph$, 644-08-6; Me_4Sn, 594-27-4; $CH_2{=}CHSnBu_3$, 7486-35-3; Ph_4Sn, 595-90-4; $PhSnBu_3$, 960-16-7; $Pd(OAc)_2$, 3375-31-3; $Pd(OCOCF_3)_2$, 42196-31-6; $Pd(dba)_2$, 32005-36-0.

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Organic Chemistry by Infrared Lasers. 4.[1] Laser-Induced Reactions of γ-Unsaturated Alcohols

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Received August 16, 1982

The laser-induced chemistry of 3-buten-1-ol (**1**), 3-butyn-1-ol (**2**), 3,4-pentadien-1-ol (**3**), 2-isopropenyl-5-methylcyclohexanol (*l*-isopulegol; **4**), and 1,5-hexadien-3-ol (**5**) is described. Retro-ene reactions occur in all cases, though with compound **5** a competitive oxy-Cope reaction is also observed. The reactions are generally clean and give rise to conversions in the range of 48–78% after 300–500 pulses. In these reactions between 2–10 photons are absorbed per molecule per pulse, and in some instances as much as 40% conversion is obtained after five pulses. The laser-induced chemistry seems to follow the known thermal chemistries of these systems.

γ-Unsaturated alcohols have received much attention in connection with thermolytic studies. These investigations originated with the liquid-phase pyrolysis of castor oil from which ricinoleic acid can be derived.[3] From this early research it was demonstrated that, depending upon the structure of the γ-unsaturated alcohols, a variety of gas-phase reactions can be accomplished. Representative examples of these reactions are illustrated in eq 1–3 and depict, respectively, a pyrolytic cleavage to olefin and carbonyl fragment,[4,5] an oxy-Cope rearrangement,[6] and a dehydrative cyclization.[7] Equation 1 is an example of the retro-ene fragmentation. This reaction has been studied

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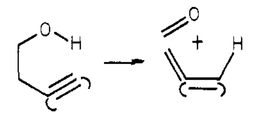
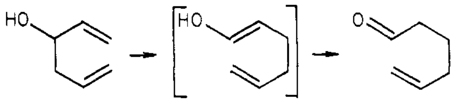


(1)



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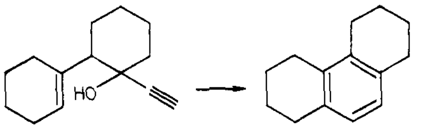

(3)

in connection with the concept of concert (as it bears a relationship to the hydrogen 1,5-sigmatropic shift) and as a synthetic route to highly substituted olefins.[8] Similarly, the oxy-Cope rearrangement shown in eq 2 has been extensively probed in its relation to the 3,3-sigmatropic shift and as a preparative method to Δ^5-unsaturated carbonyl compounds.[9]

In this investigation we report on the retro-ene reaction of several unsaturated alcohols as induced by CO_2 infrared laser radiation. In addition, a case is examined where competitive reaction pathways exist between the retro-ene cleavage and the oxy-Cope rearrangement. This study is a continuation of an ongoing effort aimed at demonstrating that organic reactions can be efficaciously promoted with use of pulsed megawatt infrared laser light. One particular advantage of laser-induced organic chemistry is the elimination, for the most part, of complicating heterogeneous surface effects. This facet of laser chemistry arises as a consequence of vibrationally excited molecules being collisionally deactivated by molecules found between the zone of irradiation and the "cold" cell walls. Thus, in principal, many reactions that are normally subject to surface effects, i.e., dehydrohalogenations,[10] ester[11] and carbamate cleavages,[12] could be investigated under more homogeneous conditions.

Experimental Section

The unsaturated alcohols studied were 3-buten-1-ol (1), 3-butyn-1-ol (2), 3,4-pentadien-1-ol (3), 2-isopropenyl-5-methylcyclohexanol (technical grade *l*-isopulegol; 4), and 1,5-hexadien-3-ol (5). Alcohols 1, 2, 4, and 5 were commercially available (Aldrich Chemical Co.), and 3 was prepared as described by Claesson et al.[13] All five substrates were irradiated under generally similar conditions, i.e., in a static system and at pressures of reactant in the range of 5–17 torr. The low vapor pressure exerted by 3 and 4 at ambient temperatures required heating the reaction cell during the irradiation. For these reactions, the cell was placed in a common drying oven and the laser beam was directed through KCl windows mounted on openings in the oven walls. In this fashion the reaction cell could be heated to temperatures in excess of 120 °C to effect vaporization. To insure that no reaction occurred as a consequence of this heating, a sample of the material was heated at the same temperature for an equivalent time period and subsequently analyzed by gas chromatography. In all cases where this vaporization method was used no reaction took place before laser irradiation.

All experiments were carried out either in a cylindrical monel cell 2.54 cm long, 30 cm^3 volume) or in a cylindrical Pyrex cell (of variable length and volume). To each cell were attached two KCl windows (3.8 cm in diameter) and a vacuum stopcock. The metal cell was used in those experiments requiring elevated temperatures. A Lumonics Research Model TEA 203, pulsed, tunable CO_2 laser was used for irradiation, and two factory calibrated Lumonics Model 200 pyrolectric detectors were used for fluence and energy absorption measurements. On some occasions, in order to achieve fluence levels above 1.5 J/cm^2, the laser beam was focused slightly with a Janos 1.5x ZnSe beam condenser. The pulse duration was approximately 150 ns and the pulse repetition rate used in these studies was 0.33 Hz.

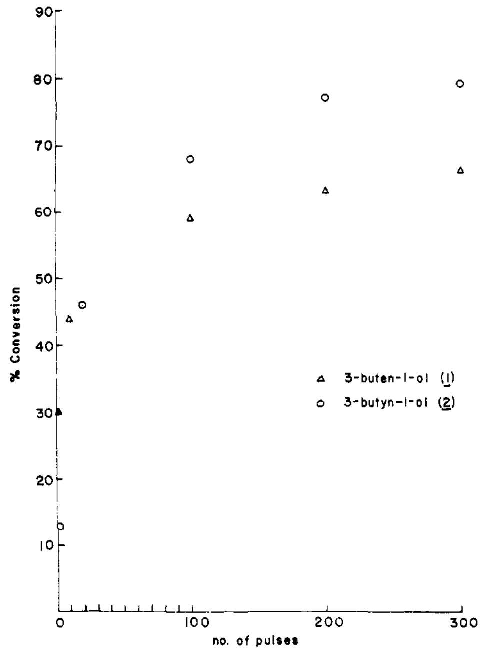

Figure 1. Percent conversion as function of number of pulses for the infrared laser induced reactions of 1 and 2.

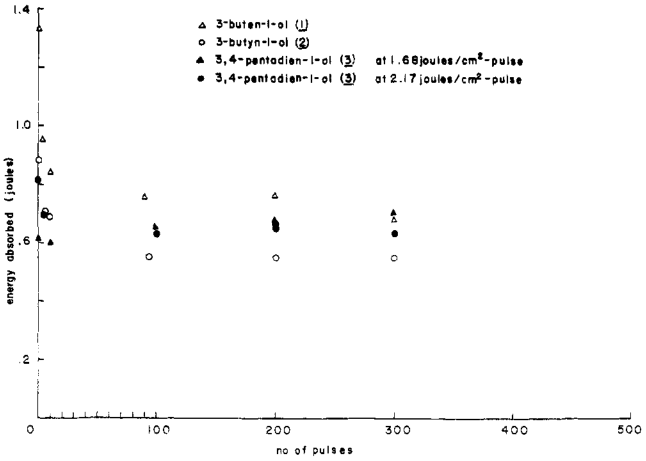

Figure 2. Energy absorbed vs. number of pulses for 1–3.

Identification of the reaction products was accomplished in all cases by comparison of the product GLC retention time and infrared spectrum with that of authentic material. To obtain percent conversion, pressure vs. absorbance plots were constructed for each of the olefinic products derived from 1–3. The plots were linear over the entire range, usually 5–50 torr. For 4 and 5, the conversion was determined by the comparison of the GLC peak areas of the reaction mixture to the GLC peak areas of known compositions of reactant and product. In the case of isopulegol (4) the percent conversion was difficult to assess since the elastomeric material of the O-rings used in the reaction cell absorbed both reactant and product.[14] Therefore, the calculated reaction

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(8) Marvel, E. N.; Rusay, R. *J. Org. Chem.* **1977**, *42*, 3336.

(9) Viola, A.; Dorio, E. J.; Chen, K. K.; Glover, G. M.; Nayak, U.; Kocionski, P. J. *J. Am. Chem. Soc.* **1967**, *89*, 3462.

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(13) Olsson, L.-I.; Claesson, A.; Bogentoft, C. *Acta Chem. Scand., Ser. B*, **1974**, *28*, 765.

(14) To preclude this problem in subsequent experiments, an all-metal cell has recently been constructed. The stainless steel cell is based on a design by Sterling and Haines[15] and differs from previous cells used in this laboratory in that the elastomeric O-rings were replaced by lead O-rings. In addition, the stem-tip of the bellows vacuum valve now consists of a stainless steel tip.

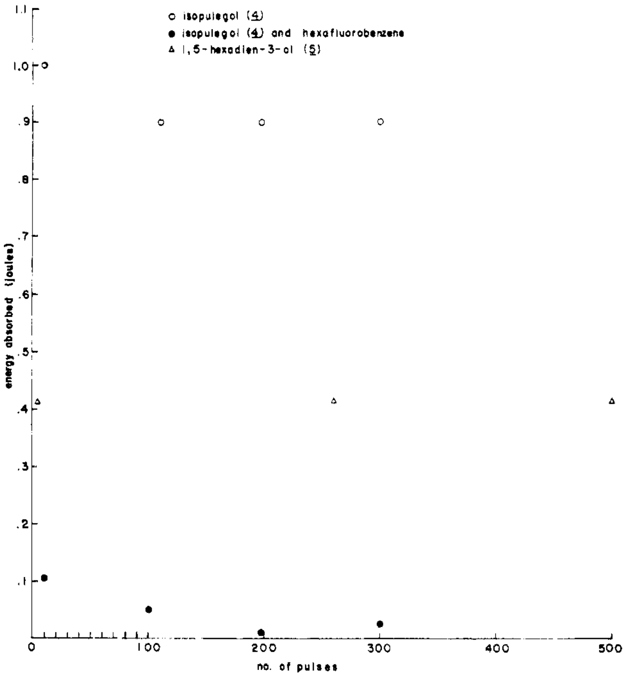


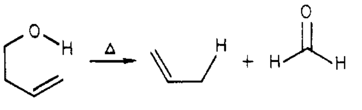
Figure 3. Energy absorbed vs. number of pulses for 4 and 5.

yield in the isopulegol experiment must be taken as a general indicator of the extent of reaction.

Results

Figures 1–3 are graphical representations of the results obtained from the infrared laser irradiation of alcohols 1–5. Figure 1 relates percent conversion of 1 and 2 to the number of pulses. Figures 2 and 3 correlate energy absorbed and number of pulses in all the reactions.

When thermolyzed at 650 K, 3-buten-1-ol (1) was reported[4] to give only propene and formaldehyde (eq 4).

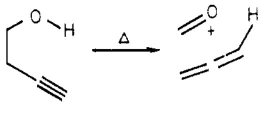


(4)

1

Similar results were observed under conditions of infrared laser irradiation. Thus, when 10 torr of 1 was irradiated at 1054 cm^{-1}, a frequency corresponding to the C–O stretch in 1, the expected products were the only ones observed. In fact, after one pulse, 30% of 1 had been converted to products. At the end of 10 pulses, infrared analysis revealed that 43% of 1 had been consumed (see Figure 1). The conversion of 1 reached 59% after 100 pulses. However, after 200 and 300 pulses the amount of decomposition of 1 changed only slightly to 63% and 66%, respectively. The average fluence delivered to the reaction cell was 1.46 J/cm^2–pulse. The amount of conversion per unit of laser pulses was also indicated by the amount of energy absorbed by the reaction system. When the conversion was the greatest, it was observed that the amount of energy absorbed was the largest, i.e., after one pulse the energy absorbed was 1.33 J (see Figure 2). Pulses 2–4 averaged 0.95 J and 5–10 averaged 0.84 J. From pulses 91–100 and 191–200 the average absorbed energy was 0.76 J. Toward the end of the experiment, pulses 291–300, the absorbed energy was 0.68 J. The initial energy absorbed corresponded to 103 kJ/mol, or an average of 8.1 photons/molecule. Although 1 appears to absorb a significant amount of energy after 300 pulses, the conversion reached a plateau by this point. This observation seems to indicate that 1 is still being activated by the laser, but before it can undergo reaction, collisional deactivation by the increased concentration of product molecules occurs.[16]

Infrared laser irradiation of 6.9 torr of 3-butyn-1-ol (2) at 1054 cm^{-1} (C–O stretch) resulted in the formation of allene and formaldehyde as the only observable products (eq 5). This behavior paralleled the thermal chemistry

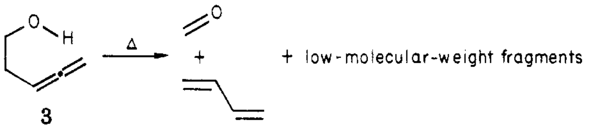


(5)

2

of 2 as reported by Viola et al.[5] After one pulse, with a fluence of 1.24 J/cm^2, the conversion was 14% (Figure 1). After 10 pulses the conversion reached 46% and after 100 pulses it had risen to 68%. A falloff in conversion appeared to have been approached between 200 and 300 pulses as it only increased from 77% to 79% in this range. The energy absorbed by 2 showed a smooth decrease from the first pulse where the absorbed energy was 0.83 J to the last pulse, which absorbed 0.53 J (Figure 2). On a per mole basis the energy absorbed during the first pulse corresponded to 81 kJ or an average 6.4 photons/molecule. It is apparent that the lower conversion of 2 relative to 1 in the initial pulse is due to the smaller energy absorbed by the former (83 vs. 103 kJ/mol) and probably can be attributed to differences in the absorbances of 1 and 2 at 1054 cm^{-1}.

The retro-ene cleavage of 3,4-pentadien-1-ol (3), induced by infrared laser radiation, did not proceed in as clean a fashion as observed for 1 and 2 (eq 6). Although form-



(6)

3

aldehyde and 1,3-butadiene were the major products of the reaction, other low-molecular-weight fragments were also observed (vide infra). This behavior paralleled the results observed in the thermolysis of 3 at temperatures above 400 °C, as reported by Madison.[17] The thermal decomposition of 3 also yielded low-molecular-weight fragments, but the author stated that they were present in insufficient quantity for identification. Infrared laser irradiation of 17 torr of 3 at 1054 cm^{-1} (C–O stretch) resulted in the formation of formaldehyde and 1,3-butadiene in 47% yield after 500 pulses. During the course of the irradiation the sample in the reaction cell was heated to 81 °C since 3 did not have a significant vapor pressure at room temperature. Since infrared analysis and further irradiation would have required the cooling and reheating of the cell and its contents, which would have affected the true concentration of formaldehyde in the vapor phase (polymerization on the cell walls and windows) and therefore the degree of collisional deactivation as compared with reactions of 1 and 2, conversion measurements were not determined from 1–200 pulses. Energy absorption measurements, however, were determined. Contrary to the behavior of 1 and 2, the absorbed energy was constant over the range of pulses and averaged 0.64 J (8.3 photon/molecule) when the fluence

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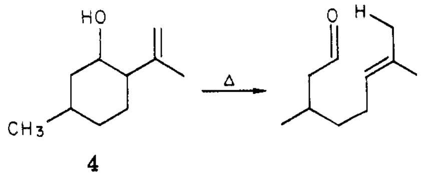
(15) Sterling, K. J.; Haines, R. J. *Anal. Chem.* **1968**, *40*, 1395.

(16) Conceivably, one could compare the initial pulse conversion of neat 1 with that observed from a mixture of 1, butene, and formaldehyde to test the above. A lower conversion would be expected after one pulse from the 1, butene, and formaldehyde mixture if collisional quenching by the product molecules is a factor.

(17) Madison, S. A. Ph.D. Dissertation, Northeastern University, Boston, MA, 1981.

was 1.68 J/(cm^2·pulse) (Figure 2). When the fluence was increased to 2.17 J/(cm^2·pulse), the absorbed energy on the first pulse was 0.81 J (10.4 photon/molecule) and decreased to an average value of 0.70 J from pulses 2–5. From the sixth to the 300-th pulse an average absorbed energy of 0.63 J was measured (Figure 2). The amount of decomposition increased significantly in this higher fluence experiment, but it was difficult to evaluate since products other than those expected from the retro-ene cleavage were observed. GC/MS indicated the products of these alternate paths to be carbon monoxide, methane, ethylene, acetaldehyde, and allene or methylacetylene. Trace amounts of CO_2 and propene were also detected by this analysis. In the low-fluence experiment these species were also observed but accounted for less than 10% of the conversion. Of all these, carbon monoxide and ethylene were the major products in both experiments.

The thermal chemistry of isopulegol (4) was first described by Grignard and Doeuvre,[18] who reported that 4 underwent 60% conversion to citronellal at 500 °C (eq 7).



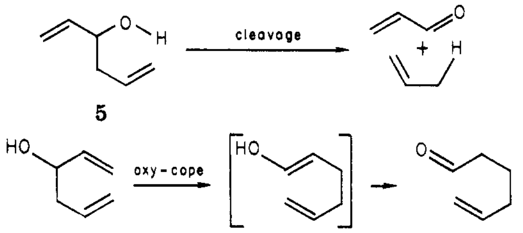
4

(7)

Subsequent studies[19] confirmed these initial findings. Initial infrared laser irradiation of 19 torr of 4 with a fluence of 1.42 J/(cm^2·pulse) did not result in any isomerization to citronellal after 250 pulses. The sample, which was heated to 91 °C, was irradiated at 1033 cm^{-1} (C–O stretch). Apparently the absence of reaction was a consequence of the relatively weak absorption of 4 at 1033 cm^{-1}. Consequently, isopulegol (4) was irradiated in the presence of a sensitizer,[20] hexafluorobenzene. This fluorinated aromatic hydrocarbon absorbs strongly at 1023 cm^{-1}, and when 9 torr of 4 and 8 torr of hexafluorobenzene were irradiated at 1023 cm^{-1}, citronellal was formed as the major product. The formation of CO, CH_4, CO_2, C_2H_4, C_2H_6, C_2H_2, C_3H_6, and other unidentified products were, however, also observed upon GLC analysis. (Vinyl fluoride was also indicated but not rigorously identified in this analysis.) The energy absorbed by the system in this experiment averaged about 1 J/pulse over the first 10 pulses and 0.9 J/pulse from pulses 90–300 (Figure 3). The possible appearance of vinyl fluoride among the reaction products, as well as the number of low-molecular-weight fragments, certainly narrows the useful limits of hexafluorobenzene as a sensitizer. It appears that this is especially true when absorbed energies of 35 kJ/mol or greater are necessary to initiate sensitized reactions.

The results were more easily interpreted, however, when the sensitizer was eliminated and the average fluence increased to 2.56 J/(cm^2·pulse). Thus, when 11 torr of 4 was irradiated at 1033 cm^{-1}, a 58% conversion to citronellal was achieved after 300 pulses. As in the previous experiment, the reaction cell containing isopulegol (4) was heated to 91 °C so as to obtain the desired vapor pressure. The amount of conversion of 4 was determined by condensing the products into a reaction-cell side-arm reservoir at 77 K, washing out the condensate with ether, and comparing this solution with known compositions of citronellal and 4 by gas chromatography. Loss of citronellal or 4 to the Viton O-rings was assumed to occur at the same rate and therefore would not add a substantial error in determining the ratio of 4 and citronellal. However, as stated above for 3, an accurate determination of the yield was a problem in this system as well. The energy absorbed per pulse appeared to decline slightly during the experiment and averaged 0.08 J (1.7 photons/molecule) for the initial 100 pulses and 0.02 J for the last 200 pulses (Figure 3).

The thermolysis of 1,5-hexadien-3-ol (5) has been reported by Viola et al.[6] and resulted in the oxy-Cope rearrangement and the retro-ene cleavage reaction (eq 8).



5

(8)

5

The product distribution obtained from this thermolysis at 375 °C indicated a 1.5:1 ratio of rearrangement to cleavage. In addition, production of cleavage products was found to predominate at higher temperatures, whereas the rearrangement was favored at lower temperatures.

Similar results were observed under conditions of infrared laser radiation. Since compound 5 showed a weak absorption in the region of the C–O stretch, the much more intense absorption band corresponding to the sp^2 C–H out-of-plane bending mode was excited. Because 5 is a "large" molecule, i.e., one that reaches the quasi-continuum after the absorption of one or two quanta, no significant differences in the reaction chemistry were expected solely on the basis of the mode excited. It is well-established that the excitation energy is essentially randomized on the multiphoton dissociation time scale.[21] In terms of reaction efficiency one could expect the conversion per pulse to vary directly with the absorbance of the particular mode excited since more energy would be absorbed. Thus, when 5 torr of 5 was irradiated at 925 cm^{-1} with an average pulse fluence of 1.39 J/cm^2, acrolein, propene, and 5-hexenal were formed. Conversion measurements after the typical number of pulses could not be determined by infrared analysis because each of the components of the reaction mixture had at least one pertinent absorption band that overlapped with those of the other components. However, GLC analysis after 500 pulses revealed that approximately 66% of 5 had reacted and also that the rearrangement to cleavage products was formed in a ratio of 1.08:1. A second experiment using similar conditions of pressure and fluence resulted in the same product distribution after 1000 pulses. Not unexpectedly, the reaction yield increased to 83% in this latter reaction. Two other products were formed in both experiments (in trace amounts) and as yet remain unidentified. As in the case of 3, the energy absorbed by 5 remained constant over the 500 pulses and averaged 0.39 J/pulse (65 kJ/mol or 5.8 photons/molecule, see Figure 3).

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(18) Grignard, V.; Doeuvre, J. *C. R. Hebd. Seances Acad. Sci.* **1930**, *190*, 1164.

(19) (a) Isikawa, S.; Tosimutu, T.; Miyata, A.; Araki, Z.; Someno, R. *Sci. Rep. Tokyo Bunrika Daigaku, Sect. A* **1939**, *3*, 273; *Chem. Abstr.* **1940**, *34*, 32403. (b) Dudley, B. D.; Williams, P. L. *Perfum. Essent. Oil Rec.* **1968**, *59*, 365; *Chem. Abstr.* **1968**, *69*, 38703u.

(20) Although silicon tetrafluoride has been used successfully as a sensitizer in many other experiments, it could not be utilized in this system since it reacts with alcohols to form silyl-oxygen compounds.

(21) (a) Oref, I.; Rabinovitch, B. S. *Acc. Chem. Res.* **1979**, *12*, 166. (b) Lussier, M.; Steinfeld, J. I. *Chem. Phys. Lett.* **1977**, *50*, 175. (c) Richardson, H.; Setser, D. W. *J. Phys. Chem.* **1977**, *81*, 2301. (d) Sudbø, A.; Schulz, P. A.; Grant, E. R.; Shen, Y. R.; Lee, Y. T. *J. Chem. Phys.* **1979**, *70*, 912. (e) Stephenson, J. C.; Bialkowski, S. E.; King, D. S.; Thiele, E.; Stone, J.; Goodman, M. F. *J. Chem. Phys.* **1981**, *74*, 3905.

Discussion

Irradiation of all the unsaturated alcohols studied gave results similar to those observed in the previously reported thermolyses. Although no definitive mechanistic arguments can be advanced, the data suggest similar modes of decomposition and isomerization in the thermal- and laser-induced reactions. The mechanism originally proposed by Arnold and Smolinsky[22] from a study of 3-ethyl-6-phenyl-5-hexen-3-[^{2}H]ol involves a cyclic array of six atoms in the transition state. Furthermore, since the reactions in cases **1**–**3** and **5** were relatively clean in terms of product formation, one can state with reasonable confidence that pathways involving homolytic cleavage do not play a significant role in these reactions.

The degree of reaction under conditions of laser irradiation is apparently fluence dependent. This was especially evident in the reaction of isopulegol (**4**) where *isomerization did not occur* (was below the limits of detection) with a fluence of 1.46 J/cm^2 but proceeded smoothly with a fluence of 2.56 J/cm^2. Additional evidence is found in the behavior of **3**. Here the energy absorbed on the first pulse was directly related to the fluence; a 29% increase in fluence resulted in an almost identical increase in the energy absorbed. Considering the high density of vibrational states probably achieved after the absorption of only a few infrared photons, these observations are not unexpected. In fact, it complements the observed differences in yield found in other multiphoton decompositions that show a fluence–yield dependence.[23]

It is also interesting to consider the possible implications of the average number of photons absorbed by **1** and **2** during the first laser pulse. There are two likely interpretations relating the average number of photons absorbed and the dissociation yield. The activation energy for the retro-ene cleavage of **1** and **2** has been reported as 40.7 and 39.9 kcal/mol,[5] respectively, which represents a reaction threshold corresponding to the absorption of approximately 13 infrared photons. In the two systems studied, significant decomposition was observed in **1** when 30% reaction occurred (an average absorption of 8.1 photons) and in **2** when 14% reaction occurred (an average absorption of 6.4 photons). Consistent with these results are relatively wide internal energy distributions as effected by the multiphoton pumping process.[24] On the other hand, since the energy absorbed by **1** and **2** on the first pulse was 30% and 21%, respectively, of the incident laser energy, inhomogeneous irradiation of the gas could account for the experimental observations. Thus, molecules at the high energy side of the reaction cell would be exposed to a higher fluence than those at the other side of the cell. Indeed, it has been reported[24] that only when the fluence change is less than 10% can $\langle n \rangle$ be calculated in a straight forward fashion from the following equation:

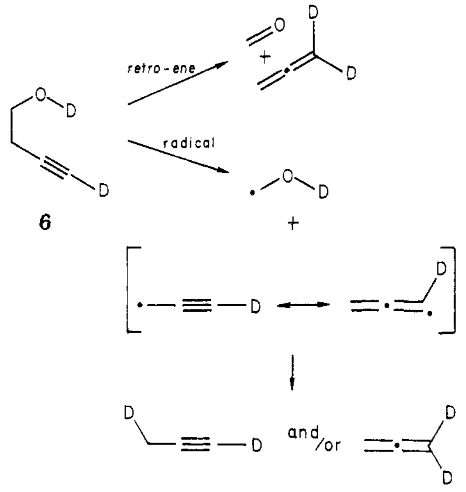
$$\langle n \rangle = \frac{\Delta E/h\nu}{[\text{reactant}]\,V_{\text{irr}}}$$

where $\langle n \rangle$ = average number of photons absorbed per molecule, ΔE = absorbed energy, [reactant] = molecules/cm^3, and V_{irr} = volume irradiated in cubic centimeters. In any event, high absorbed energies and a minimum number of pulses seem to be required if laser-induced reactions are to be of practical synthetic utility. Of course, a limit would be approached when these high levels of excitation begin to induce, competitively, pathways of higher energetic demands. A particular advantage to completing the reaction with a small number of pulses is that product molecules would suffer a diminished likelihood of secondary decomposition.

If one assumes that, in the laser-irradiated experiment, **5** reacts from a thermally equilibrated system, then the product ratio allows one to qualitatively define the reaction temperature attained in the system. Since the laser reaction yielded more cleavage relative to rearrangement than in the reported thermolysis, and since it was also reported that higher temperatures favor the cleavage process, one must conclude a laser reaction temperature in excess of 375 °C. How much higher than 375 °C is, however, difficult to ascertain since the necessary parameters, A and E_a (the Arrhenius frequency factor and activation energy, respectively), are not available for the two competitive processes in **5**.

It should be noted that the cleavage products can result from both a direct retro-ene reaction and from secondary decomposition of the oxy-Cope rearranged product, 5-hexenal. This was a distinct possibility in the laser process since 5-hexenal has an infrared absorption band at the irradiating frequency. If secondary decomposition of 5-hexenal is significant, then this could account for the decreased rearrangement/cleavage ratio as observed in the laser reaction. However, the rearrangement/cleavage ratio remained constant after 500 and 1000 pulses and therefore the contribution of acrolein and propene from 5-hexenal decomposition is probably small after the first 500 pulses. The above conclusion cannot be drawn in the earlier stages of the reaction.

In summary, the retro-ene and oxy-Cope reactions appear to be a fertile area for infrared laser studies. In particular, the laser method can be used to probe aspects of synthetic utility and reaction mechanism. Further studies are aimed at defining the contribution if any of laser-generated radical intermediates in these systems. For instance, the doubly deuterated alcohol **6** should result in some 1,3-dideuteriopropyne and/or some species other than 1,1-dideuterioallene *if a discrete radical is involved* as depicted in eq 9, while only 1,1-dideuterioallene should result if a concerted retro-ene reaction takes place.



6 (9)

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Registry No. **1**, 627-27-0; **2**, 927-74-2; **3**, 5557-87-9; **4**, 89-79-2; **5**, 924-41-4.

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