Organic Chemistry by Infrared Lasers. 2.[1]
Retro-Diels–Alder Reactions[2]

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Abstract: Norbornadiene, cyclohexene, 4-vinylcyclohexene, *d*-limonene, and 2,3-dihydropyran undergo laser-induced retro-Diels–Alder reactions at ambient temperature in the presence of SiF_4 when irradiated at 1025 cm^{-1} by a pulsed megawatt CO_2 laser. The reaction cell never gets warm. Norbornadiene affords cyclopentadiene and acetylene along with toluene and, in some experiments, benzene. Lower pressures of sensitizer (SiF_4) afford better yields of diene and dienophile at the expense of other products. Cycloheptatriene is not observed under any conditions. Compared with the large number of compounds observed in its thermal reaction, the reaction with cyclohexene is very clean and affords only acetylene and methane along with the usual diene and dienophile. Acetylene and methane are shown to be secondary decomposition products of the diene and dienophile. Vinylcyclohexene, which is stable up to 650 °C, cleanly undergoes the laser-induced decomposition. The reaction with *d*-limonene is also clean and more efficient than that previously done under CW laser conditions. In the case of 2,3-dihydropyran, both direct irradiation at 1072 cm^{-1} and sensitized initiation at 1025 cm^{-1} with SiF_4 afford acrolein and ethylene exclusively. These reactions are examples of the "cold pyrolytic" process which seems typical of laser-induced reactions.

Recently there has been great interest in the development of the use of infrared lasers to induce and augment chemical reactions. While the prospects for carrying out syntheses by this method are unclear at present, there have been a number of published examples which demonstrate the utility of this method in isomerization[1,3,4] and degradation.[5,6] Yogev and co-workers,[7] in an early example of laser degradation, showed that *l*-limonene could be induced to undergo a retro-Diels–Alder reaction to give isoprene when irradiated at 943 cm^{-1} with a low-power CW CO_2 laser. Though no quantitative data were given, other products were also formed. They included those derived from isoprene decomposition and a minimum of six products which were probably derived from limonene itself (benzene, toluene, ethylbenzene, methylethylbenzene, allo-ocimene, and dehydrolimonene). We have been studying the utility of pulsed, megawatt CO_2 lasers applied to organic transformations and herein report our results on the retro-Diels–Alder reaction of *d*-limonene (**4**), norbornadiene (**1**), cyclohexene (**2**), 4-vinylcyclohexene (**3**), and 2,3-dihydropyran (**5**). In doing so we wish to emphasize the simplicity and practical utility of the laser method as well as control in minimizing secondary decompositions. Since the retro-Diels–Alder reaction has recently been used to generate important precursors for the synthesis of a large variety of medically important prostanoids,[8] this efficient method of laser-induced decomposition represents an important and timely addition to the aresenal of techniques useful for molecular transformation.

Experimental Section

All experiments were carried out in a cylindrical monel cell (2.6 cm long, 17 cm^3 volume) which was lined with Teflon. The cell was fitted with NaCl windows (3.8 cm in diameter) and a vacuum stopcock. Cells were filled with reactants using standard vacuum line techniques. A Lumonics Research Model TEA 103, pulsed, tunable CO_2 laser was used for irradiation and a factory-calibrated Lumonics Model 20D pyroelectric detector was used for energy measurements. A Scientech disc calorimeter was used for a calibration standard. The pulse duration was measured with a photon drag detector and was found to be ~290 ns. (Pulse width at half light is 80 ns, and ⅔ of the energy is delivered during the first 200 ns.) The laser beam was not focused and power levels of between 0.1 and 10 MW/cm^2 were achieved. Reactions were monitored before and after irradiation with a Perkin-Elmer Model 567 infrared spectrophotometer and products were identified by comparison of infrared spectra and GLC retention times with those of authentic samples. Quantitative data (percent composition) of the reaction mixtures were obtained by GLC (Varian Model 1700 with thermal conductivity detectors) and, when possible,

compared with quantitative infrared data. Poropak N (6 ft) and SE-30 (5 ft) columns were used in all separations and identifications. Gas samples from the reaction cell were introduced directly into the gas chromatograph using a Varian six-port valve. All gases were purchased from Matheson and used without further purification. Cyclohexene, vinylcyclohexene, norbornadiene, *d*-limonene, and 2,3-dihydropyran were distilled and degassed prior to use. A typical experiment, from filling the cell to identifying products, took about 0.5 h.

Results and Discussion

The five retro-Diels–Alder reactions studied are shown below. All of the starting adducts except **5** have negligible
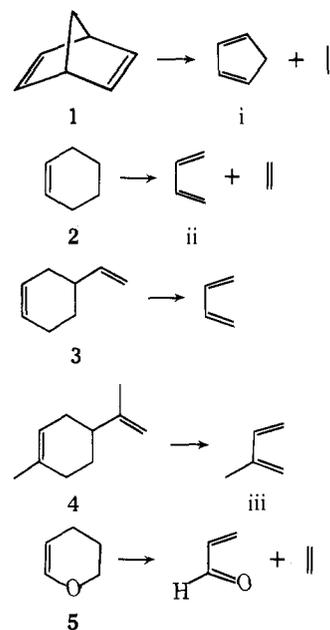
absorptions in the 9.2–11-μ output region of the CO_2 laser and therefore a sensitizer, SiF_4,[9] was used. SiF_4 has a strong triply degenerate Si–F stretching mode centered at 1032 cm^{-1} and tuning the CO_2 laser to 1025 cm^{-1} afforded excellent energy absorption by the SiF_4. The conditions and results for the various substrates are summarized in Table I.

In all the reactions involving SiF_4 the energy absorbed by the SiF_4 is 30–50% of the incident energy while the number of flashes ranged from 1 to 100. Products could be observed after one flash when high SiF_4 pressures were used. In some cases the entire reaction was over in five to ten flashes. Low SiF_4

Table I[a]

compd	pressure, Torr (substrate)	pressure, Torr[b] (SiF$_4$)	dose/ flash, J/cm^2	no. of flashes	% rxn	products: Torr (%)[e]					
						diene	dieno phile	CH$_4$	C$_2$H$_2$	C$_2$H$_4$	other
1	12.5	5.5	0.30	50	100	8.9 (40.7)	see C$_2$H$_2$		9.7 (44.1)		toluene; 3.7 (15.3)
		2.19	0.52	12	96.1	5.3 (19.5)	see C$_2$H$_2$		15.5 (57.6)		benzene; 1.9 (7.0) toluene; 4.3 (15.9)
	20	30	0.53	1	64.4	5.3 (16.3)	see C$_2$H$_2$		25.6 (78.1)		toluene; 1.9 (5.7)
2	10	6	0.23	100	100	6.0 (31.9)	see C$_2$H$_4$	0.8 (4.3)	2.8 (15.1)	9.1 (48.6)	
3	6	6	0.21	10	48.8	4.9 (87.9)	see diene		0.7 (12.3)		
4	c	9	0.37	100	d	11.7 (76.7)	see diene	1.2 (8.0)	0.4 (2.3)	2.0 (12.9)	
5	18.5	5	~0.3	3	33.2	5.86 (50)	5.86 (50)				
	14	0	0.14	100	34.3	4.8 (50)	4.8 (50)				
	33	0	0.25	100	65.7	21.2 (50)	21.2 (50)				
	16	0	~0.3	2	32.5	5.1 (50)	5.1 (50)				

[a] Irradiation at 1025 cm^{-1} in all reactions containing SiF$_4$. Those without SiF$_4$ were irradiated at 1072 cm^{-1}. [b] At high SiF$_4$ pressures carbon deposits were frequently observed on the cell walls after irradiation. [c] 0.34 mL of liquid injected into cell. [d] Percent reaction is not calculated because there was always liquid limonene left after irradiation. [e] Error limits, ±1 to ±5%.

Table II[a]

compd	pressure, Torr (substrate)	pressure, Torr (SiF$_4$)	dose/ flash, J/cm^2	no. of flashes	% rxn	products: Torr (%)[d]			
						CH$_4$	C$_2$H$_4$[b]	C$_2$H$_2$[c]	other
i	10	13	0.30	50	68.3	1.0 (7.4)		11.5 (85.0)	benzene 1.0 (7.4)
ii	16	7	0.25	60	51.4	1.4 (8.3)	4.7 (27.9)	10. (59.9)	benzene 0.64 (3.8)
iii	10	18	0.20	25	73.1	3.26 (16.4)	4.0 (19.6)	12.7 (64.0)	

[a] Irradiation at 1025 cm^{-1}. [b] Irradiation of ethylene (20 Torr) with SiF$_4$ (11 Torr) afforded acetylene, methane, and benzene. [c] Irradiation of acetylene (17 Torr) with SiF$_4$ (12 Torr) afforded benzene and carbon. [d] Error limits, ±1 to ±5%.

pressures were generally used since secondary decomposition of diene and dienophile took place at high SiF$_4$ pressures. Table II summarizes the results of the irradiation of a number of dienes in the presence of SiF$_4$.

In the laser-induced degradation of norbornadiene the major products at low SiF$_4$ pressure were cyclopentadiene and acetylene. A little more than the stoichiometrically expected amount of acetylene was observed owing to the secondary decomposition of cyclopentadiene. Indeed, when cyclopentadiene was irradiated the major decomposition product was acetylene.

The only other product detected during the laser-induced retro-Diels–Alder reaction of norbornadiene is toluene.[10] Its presence in this reaction and absence in the decomposition of cyclopentadiene alone indicate that it probably arises via a competitive isomerization pathway. This analysis conforms to the known thermal and ultraviolet photochemical behavior of norbornadiene.[11-19]

It is interesting to point out that in both the thermolysis and the ultraviolet photochemical decomposition of norbornadiene, cycloheptatriene was an observed product. None was ever detected in our laser-induced reaction. In addition, the amount of toluene formed by our method was much less.[16] Thus, by the laser-induced method we were able not only to minimize secondary decompositions but also to reduce competitive reaction pathways to the retro-Diels–Alder reaction.

The results obtained on cyclohexene, 4-vinylcyclohexene, and *d*-limonene were similar to those of norbornadiene, except that no competitive isomerizations took place (see Tables I and II). For cyclohexene, the increased amount of dienophile, ethylene, and the presence of methane and acetylene is again attributable to secondary decomposition. Compared with the thermal chemistry of cyclohexene the above results are impressive. Thermolysis[20] of cyclohexene at temperatures of 425–535 °C affords, along with ethylene and butadiene, methane, ethane, butane, hexane, isohexane, cyclopentadiene, cyclohexadiene, benzene, and a number of other compounds. It should be noted that all of the laser-induced retro-Diels–Alder reactions described here were carried out at room temperature and during irradiation the reaction cell never became warm;[21] thus a "cold pyrolysis" was actually carried out. This "cold pyrolytic" method may prove to be of technical importance since substrates and products are never subjected to continuous heating which usually gives rise to undesired products.[22]

The reaction of vinylcyclohexene was very clean and afforded excellent yields after ten pulses. Using fewer pulses minimized secondary decompositions,[23] and suggests, along with the data for the other reactions, that maximum efficiency for the retro-Diels–Alder reaction will not only occur at low SiF$_4$ pressure but also when few pulses are used.

Two very interesting features should be noted concerning

the reaction with d-limonene. Firstly, as stated above, Yogev and co-workers[7] found numerous decomposition products besides isoprene and those derived from isoprene under CW conditions. We, on the other hand, observed only isoprene (77%) and its decomposition products; thus, the pulsed megawatt method is more selective.[24] Secondly, unlike norbornadiene, cyclohexene, and 4-vinylcyclohexene, which were introduced as gases into the irradiation cell, d-limonene was injected as a liquid into the cell, so that liquid material remained in the cell during the reaction. Limonene has a vapor pressure at ambient temperature (2–3 mm) and as it reacts (in the gas phase), more limonene vaporizes. This feature can be of use in carrying out laser retro-Diels–Alder reactions on liquids and large quantities of material which have low vapor pressure, and would be very conducive for a flow system technique.[25]

When **5** was irradiated in the presence of SiF_4 at 1025 cm^{-1} (where the energy absorbed is between 30 and 50% of the incident energy) after three pulses, a 33% conversion was realized. Acrolein and ethylene were formed exclusively in their stoichiometric quantities.[26] Since 2,3-dihydropyran has a strong C–O stretching absorption at 1075 cm^{-1} a comparison of the direct and sensitized reactions was made. The result of direct irradiation of the pyran **5** in the absence of sensitizer was similar to that with sensitizer. From a mechanistic point of view, these reactions are most intriguing. They both yielded the same products at approximately the same rate yet the direct reaction was initiated when 2,3-dihydropyran absorbed the energy, while the sensitized reaction was initiated when SiF_4 absorbed the energy. We are presently studying the kinetics of these interesting reactions in collaboration with Professor E. Grunwald in order to determine energy transfer pathways and reaction mechanism.

Since the retro-Diels–Alder reaction has a variety of applications in organic and physical organic chemistry,[11] particularly in the generation of unstable intermediates[27] and in the preparation of unusual molecules,[28] and since it is of fundamental theoretical interest,[29] the laser method of degradation can offer much in the way of synthetic utility and mechanistic studies. We are continuing our studies in this exciting field.

References and Notes

(1) For previous paper in this series see C. Cheng and P. M. Keehn, *J. Am. Chem. Soc.*, **99**, 5808 (1977).
(2) Work supported by Research Corporation and the National Science Foundation.
(3) I. Glatt and A. Yogev, *J. Am. Chem. Soc.*, **98**, 7087 (1976).
(4) A. Yogev and R. M. J. Benmair, *Chem. Phys. Lett.*, **46**, 296 (1977).
(5) W. C. Danen, W. D. Munslow, and D. W. Setser, *J. Am. Chem. Soc.*, **99**, 6961 (1977).
(6) J. N. Butler, *J. Am. Chem. Soc.*, **84**, 1343 (1962).
(7) A. Yogev, R. M. J. Loeweinstein, and D. Amar, *J. Am. Chem. Soc.*, **94**, 1091 (1972).
(8) J.-B. Wiel and F. Rousessac, *J. Chem. Soc., Chem. Commun.*, 446 (1976).
(9) K. J. Olszyna, E. Grunwald, P. M. Keehn, and S. P. Anderson, *Tetrahedron Lett.*, 1609 (1977).
(10) Irradiation of toluene (10 Torr) with SiF_4 (5 Torr) afforded less than 2 Torr acetylene after 50 flashes. With 24 Torr SiF_4, after 10 flashes, small amounts (2–3 Torr) of acetylene and benzene were observed along with elemental carbon.
(11) K. Kwart and K. King, *Chem. Rev.*, **68**, 415 (1968).
(12) B. C. Roquitte, *J. Am. Chem. Soc.*, **85**, 3700 (1963).
(13) B. C. Roquitte, *J. Phys. Chem.*, **69**, 2475 (1965).
(14) W. C. Herndon and L. L. Lowry, *J. Am. Chem. Soc.*, **86**, 1922 (1964).
(15) H. R. Willcott and E. Goerland, *Tetrahedron Lett.*, **51**, 6341 (1966).
(16) W. G. Woods, *J. Org. Chem.*, **23**, 110 (1958).
(17) J. H. Birely and J. P. Chesick, *J. Phys. Chem.*, **66**, 568 (1962).
(18) B. C. Roquitte, *Can. J. Chem.*, **42**, 2134 (1964).
(19) R. Walsh and J. M. Wells, *J. Chem. Thermodyn.*, **7**, 149 (1975).
(20) S. R. Smith and A. S. Gordon, *J. Phys. Chem.*, **65**, 1124 (1961).
(21) T/R temperatures of the gas mixture within the beam have been calculated to be in the 1000–1500 K range.
(22) The cleanliness of these reactions is due at least in part to the fact that there are no wall effects entering into the reaction. This is because the laser beam is smaller than the diameter of the reaction cell; about 70% of the cell volume is irradiated.
(23) 4-Vinylcyclohexene is stable up to 644 K. See (a) S. W. Benson, *J. Chem. Phys.*, **46**, 4920 (1967); (b) G. B. Kistiakowsky and W. W. Ranson, *ibid.*, **7**, 725 (1939).
(24) Along with isoprene (6%) the pyrolysis of d-limonene at 450 °C afforded a variety of aromatic compounds (7%), and nonaromatic hydrocarbons (77%) which were mostly dienic. See H. Pines and J. Ryer, *J. Am. Chem. Soc.*, **77**, 4370 (1955).
(25) Considering the possibility for reaction in the condensed phases (liquid and solid), it should be noted that we were able to decompose sulfolene (a solid) in the presence of SiF_4. However, the pressure of SiF_4 (28 Torr) required for the retro-Diels–Alder reaction did not allow us to detect the primary retro-Diels–Alder product of butadiene. Sulfur dioxide, methane, ethylene, and acetylene were observed in the reaction. We believe that the latter three compounds represent the secondary decomposition of the butadiene which formed in the reaction but could not survive the conditions of high SiF_4 pressure.
(26) Thermally, 2,3-dihydropyran afforded only ethylene and acrolein at temperatures between 316 and 510 °C. Above these temperatures other products were observed: (a) C. A. Wellington, *J. Chem. Soc. A*, 2584 (1969); (b) D. G. Retzloff, B. M. Coull, and J. Coull, *J. Phys. Chem.*, **74**, 2455 (1970).
(27) E. J. Corey and W. L. Mock, *J. Am. Chem. Soc.*, **84**, 685 (1962).
(28) T. J. Katz, M. Rosenberger, and R. K. O'Hara, *J. Am. Chem. Soc.*, **86**, 249 (1964).
(29) R. B Woodward and R. Hoffmann "The Conservation of Orbital Symmetry", Verlag Chemie, Weinheim/Bergstr., Germany, 1970.