# Gas-Phase Thermolysis of 1,5-Hexadiene: The Continuous Wave CO_2 Laser-Induced Reaction and Studies of the Cyclization Pathway

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Abstract: The continuous wave CO_2 laser-induced chemistry of 1,5-hexadiene has been studied at low pressures and at laser powers between 40 W/cm², the threshold for reaction at 40 torr, and 125 W/cm². Irradiation of a 40-torr sample at 100 W/cm² to 85% conversion gave methane (4.4%), ethene (14%), ethyne (7%), propene (46%), 1,2-propadiene (2.1%), 1-butene (8.1%), 1,3-butadiene (6.6%), 1,3-cyclopentadiene (2.7%), and benzene (5.9%) along with several minor and trace products. The hexadienyl radical **1** is a likely cyclization intermediate. However, 4-methylcyclopentene, the major product expected from cyclization of **1** and hydrogen abstraction, is present to the extent of less than 0.1%, suggesting that this radical cyclization pathway is either unimportant or the cyclopentenylmethyl radical undergoes rapid reversion to **1**. Radical **1** has been independently prepared in the gas phase and in solution, and products of its reactions have been identified. In the gas phase, **1** appears to principally undergo hydrogen atom loss giving (*E*)- and (*Z*)-1,3,5-hexatriene which, under the conditions employed, give 1,3-cyclohexadiene. In solution **1** gives 1,4- and 1,5-hexadiene (60.6%) and 4-methylcyclopentene (37.3%), but no cyclohexene. The mechanisms of formation of cyclic products upon pyrolysis of 1,5-hexadiene are discussed in light of the results obtained. Factors accounting for the observed differences between solution and gas-phase products are also discussed.

The gas-phase pyrolysis of 1,5-hexadiene (diallyl) is a fascinating process which results in aromatization of a portion of the starting material.[1-3] The main products observed are propene, benzene, ethylene, 1,3-butadiene, 1,3-cyclopentadiene, 1-butene, cyclopentene, and 1,3-cyclohexadiene. Aside from the significant practical interest in aromatization processes,[4] there are important mechanistic considerations, especially regarding the possible cyclization pathways. Allyl radicals, having been mass spectroscopically identified[5,6] and chemically trapped[1] upon heating 1,5-hexadiene, are mechanistically implicated. It is generally accepted[2,3] that allyl radicals initiate cyclization by reacting with 1,5-hexadiene to form the substituted allyl radical **1**, eq 1 and 2.

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(2)
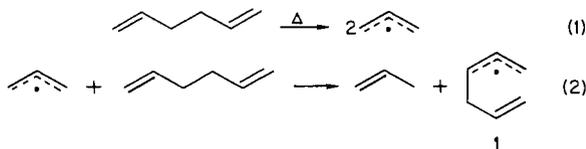
Benzene has been proposed to arise by two routes. Ruzicka and Bryce[2] suggested that radical **1** undergoes cyclization followed by hydrogen loss, eq 3 and 4. They assumed, but did not observe, cyclohexadiene intermediates. Nohara and Sakai[3] did identify

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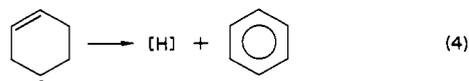
1,3-cyclohexadiene as a secondary product and proposed that **1** initially gives the hexatrienes, eq 5. The *cis*-triene readily ring closes, eq 6. Isomerization of the *trans*- to the *cis*-triene, eq 7, which is known to occur at high temperatures,[7,8] is proposed to complete the sequence. To support their mechanism Nohara and Sakai identified 1,3,5-hexatriene as a minor product whose yield decreases with increasing conversion. They also cited the work of James and Troughton,[9] who observed the dependency of

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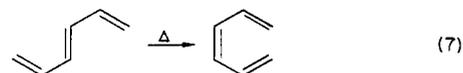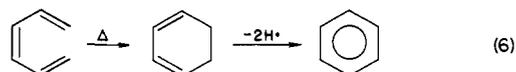
1,3,5-hexatriene and 1,3-cyclohexadiene yields on temperature. Thus, the Nohara–Sakai mechanism is more firmly established than the one proposed by Ruzicka and Bryce.

Do the two mechanisms compete? It is now well established that 5-hexenyl radicals rapidly cyclize, but five- rather than six-membered rings are preferred.[10-12] Therefore, a cursory assessment may suggest that, if the Ruzicka–Bryce mechanism is occurring, products from the five-membered cyclic radical, eq 8, rather than from the six-membered cyclic radical, eq 3, should

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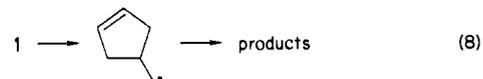
be present. Cyclopentene and 1,3-cyclopentadiene could be postulated to arise via eq 8; however, other routes are proposed.[2,3]

We have sought evidence for duality of mechanism by (i) carefully examining the products from the laser-assisted gas-phase

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(1) Akers, R. J.; Throssell, J. J. *Trans. Faraday Soc.* **1967**, *63*, 124.

(2) Ruzicka, D. J.; Bryce, W. A. *Can. J. Chem.* **1960**, *38*, 827.

(3) Nohara, D.; Sakai, T. *Ind. Eng. Chem. Prod. Res. Dev.* **1973**, *12*, 322.

(4) Aromatization of hexadienes is typically a metal-catalyzed process, cf.: Isagulyants, G. V.; Dubinskii, Y. G.; Rozengart, M. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1981**, *2*, 462. Paal, Z.; Tetenyi, P. *J. Catal.* **1973**, *30*, 350.

(5) Lossing, F. P.; Ingold, K. U.; Henderson, I. H. *J. Chem. Phys.* **1954**, *22*, 621.

(6) Bryce, W. A.; Ruzicka, D. J. *Can. J. Chem.* **1960**, *38*, 835.

(7) Rose, T. L.; Seyse, R. J.; Crane, P. M. *Int. J. Chem. Kinet.* **1974**, *6*, 899.

(8) Orchard, S. W.; Thrush, B. A. *J. Chem. Soc., Chem. Commun.* **1973**, *14*.

(9) James, D. G. L.; Troughton, G. E. *Trans. Faraday, Soc.* **1966**, *62*, 145.

(10) Beckwith, A. L. *J. Tetrahedron* **1981**, *37*, 3037.

(11) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317.

(12) This preference was unknown when the Ruzicka–Bryce article appeared and later workers have not discussed it. For an historical overview, see: Wilt, J. W. In "Free Radicals"; J. Kochi, Ed.; New York: Wiley, 1973.

pyrolysis of 1,5-hexadiene under varying conditions, (ii) independently preparing radical **1** in the gas phase and in solution and observing the products produced, and (iii) subjecting *cis*- and *trans*-1,3,5-hexatriene to the same conditions used for 1,5-hexadiene.

Experimental Section

Materials. 1,5-Hexadiene and 1,3,5-hexatriene (mixture of ca. 40% cis and 60% trans by GC) were obtained commercially (Aldrich) and used without further purification. 3-Bromo- and 3-chloro-1,5-hexadiene were custom products (Zutaut Specialty Chemicals) and were found by GC and NMR analysis to be mixtures of cis- and *trans*-6-halo-1,4-hexadiene and the 3-halo-1,5-hexadiene isomer. The mixtures were used for the experiments described. Tri-*n*-butylstannane was purchased (Alfa) and stored at −20 °C until used.

Infrared Spectra and Gas Chromatography. IR spectra were collected on a Mattson Sirius 100 FT-IR spectrometer equipped with a KBr/Ge beamsplitter and a triglycine sulfate (TGS) detector. Interferograms were transformed after applying a triangular apodization function with an effective spectral resolution of 1.0 cm^{-1}. This resolution was sufficient to allow unequivocal identification of products and (unreacted starting material) from characteristic IR frequencies, provided that the product has absorption bands which were unobscured by other products or reactant. The following products were identified by their characteristic IR bands (cm^{-1}): methane (1306),[13] ethene (949),[13] ethyne (729),[13] propene (912, 990),[14] propyne (633, 1249, 3334),[15] 1,2-propadiene (800–900),[16] 1,3-butadiene (908),[17] 1,3-cyclopentadiene (664),[18] 1,3-cyclohexadiene (658),[19] benzene (674, 1038),[13] *trans*-1,3,5-hexatriene (899).[20]

GC analyses were performed at low temperatures on a Hewlett-Packard Model 5840A chromatograph equipped for liquid CO_2 cooling and with a 15 m OV 101-coated capillary column. Analyses above ambient were routinely performed on a Varian Model 4600 chromatograph with a 25 m OV 101-coated capillary column. Each instrument utilized a flame ionization detector and was operated in a split mode. Peaks were electronically integrated, and the percentages reported are response corrected. Temperature-programmed runs starting at −40 °C were utilized to separate the main components of the 1,5-hexadiene and halo-1,5-hexadiene reaction mixtures. All components identified in Tables I and II were confirmed by the use of authentic samples except as stated. Ethene and ethyne could not be separated at −40 °C with the column used. However, the ethyne–ethene composition was determined by use of the FT–IR spectrum of the products and composition calibration curves for the components. Propyne was also identified by FT–IR and assigned in the GC chromatogram based on its assumed retention time as compared to the other standards.

Laser Photochemical Experiments. IR laser excitation in the range of the C═C—H out-of-plane bending vibration was provided by a coherent Radiation Laboratories Model 41 continuous wave (CW) CO_2 laser. The exact laser frequencies were verified with an Optical Engineering CO_2 spectrum analyzer. In single-line operation, output powers up to 150 W could be obtained by varying the current and the (CO_2–N_2–He) gas mixture in the laser tube. Laser irradiation times were controlled by a clock-operated solenoid (0.1 s time intervals).

1,5-Hexadiene exhibits IR absorption between 1050 and 890 cm^{-1} with the most intense vibration between 940 and 890 cm^{-1}. The P(36) [00°1 − 10° 0] line of the CO_2 laser at 929.02 cm^{-1} is resonant with this band and was the main excitation frequency used in this study. Laser irradiation powers were varied from 25 to 125 W/cm^2 and irradiation times from 0.2 to 40 s were used. The 1,5-hexadiene sample pressure was normally ca. 40 torr before irradiation.

The P(40) line at 924.97 cm^{-1} was used to irradiate samples of the bromo- and chlorohexadienes and 1,3,5-hexatriene. Because of its low vapor pressure, the concentration of the bromohexadiene was much lower (ca. 4 torr) than normal; therefore, although the bromohexadiene sample reacted, conversion was low.

(13) Herzberg, G. "Infrared and Raman Spectra"; Van Nostrand-Reinhold: New York, 1945.

(14) Gross, B.; Forel, M. T. *J. Chem. Phys.* **1965**, *62*, 1163.

(15) (a) Thomas, R. K.; Thompson, H. W. *Spectrochim. Acta.* **1969**, *24A*, 1338. (b) Thomas, R. K.; Thompson, H. W. *Ibid.* **1968**, *24A*, 1354. Kalinski, V. F.; Little, T. S. *J. Raman Spectrosc.* **1983**, *14*, 253.

(16) Mills, I. M.; Smith, W. L.; Duncan, J. L. *J. Mol. Spectrosc.* **1965**, *16*, 349.

(17) Sverdlon, L. M.; Tarasova, N. V. *Opt. Spectrosc.* **1960**, *9*, 159.

(18) Gallinella, E.; Fortunato, B.; Mirone, D. *J. Mol. Spectrosc.* **1967**, 24, 345.

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(20) Lippincott, E. R.; White, Z. E.; Sibilia, J. P. *J. Am. Chem. Soc.* **1958**, *80*, 2926.
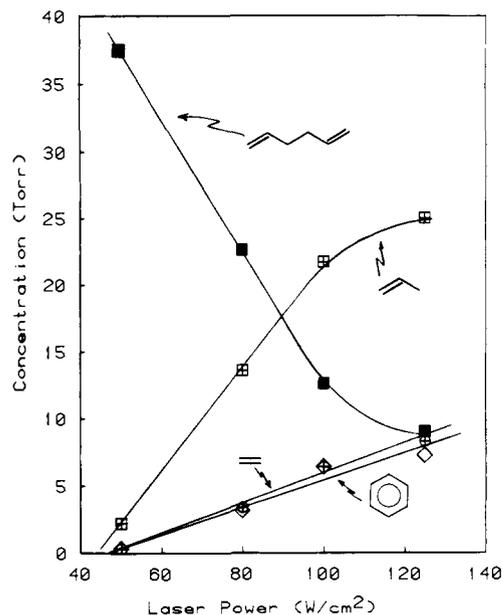
Figure 1. Plot of concentration of 1,5-hexadiene, propene, ethene, and benzene after reaction of 1,5-hexadiene (40 torr) at various laser power levels with a total energy input of 1000 J.
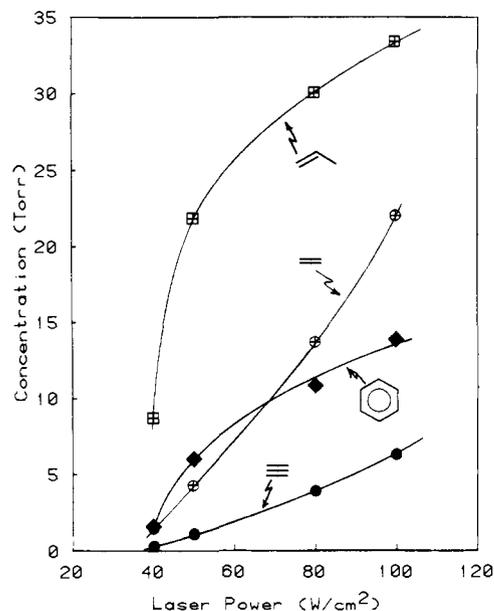
Figure 2. Plot of concentration of propene, ethene, benzene, and ethyne after reaction of 1,5-hexadiene (80 torr) at various laser power levels with a total energy input of 1000 J.

Reaction of 1 in Solution. Following published procedures,[21] the isomeric mixture of (*E*)- and (*Z*)-6-bromo-1,4-hexadiene and 3-bromo-1,5-hexadiene (0.61, 3.8 mmol), tri-*n*-butylstannane (1.1 g, 3.8 mmol), and azobisisobutyronitrile (2 mg) was dissolved in phenyl ether (10 mL) in a thick-walled glass reaction vessel. The solution was degassed (freeze–thawed), sealed, and heated to 100 °C for 4 h. GC analysis of the resulting solution revealed the following yields of products: 4-methylcyclopentene (37.3%), cyclohexene (<0.1%), 1,5-hexadiene (17.9%), (*E*)- and (*Z*)-1,4-hexadiene (42.7%), and minor products (2.1%).

Results and Discussion

1,5-Hexadiene (40 torr) was irradiated at 1000 J at various CO_2 laser power levels, and the IR spectrum was obtained. From these experiments and a series of concentration vs. IR peak height curves, a plot of the laser power vs. concentration of 1,5-hexadiene,

(21) Beckwith, A. L. J.; Easton, C. J.; Lawrence, T.; Serelis, A. K. *Aust. J. Chem.* **1983**, *36*, 545.

Table I. Products of Laser-Assisted Reaction of 1,5-Hexadiene[a]

GC retention time (min)[b]	structure	% of product	GC retention time (min)[b]	structure	% of product
0.81	CH_4	4.4	3.18	(structure)	2.7
0.81	$CH_2=CH_2$	14[c]	3.69	(structure)	0.2
0.81	$CH\equiv CH$	7[c]			
0.88	$CH_3CH=CH_2$	46.0	4.92	(structure)	trace
0.94	$CH_2=C=CH_2$	2.1	5.32	(structure)	<0.1
0.94	$CH_3C\equiv CH$	0.4	6.11	(structure)	0.2
1.14	(structure)	8.1	6.23	g	trace
1.14	(structure)	6.6	6.43	(structure)	5.9
1.26	d	0.2	6.70	(structure)	0.7
1.35	e	trace	6.80	(structure)	0.4[h]
2.00	f	0.6	6.95	(structure)	trace
2.18	(structure)	0.4	8.95	i	0.1

[a] From a reaction of 40 torr of 1,5-hexadiene irradiated with 100 W/cm^2; reaction was 85% complete based on unreacted 1,5-hexadiene at 4.58 min. [b] Retention times from a run starting at −20 °C with a 3-min hold and then programmed with a 10 deg/min increase. [c] Approximate yields based on GC and IR analysis. [d] Probably *trans*-2-butene. [e] Probably *cis*-2-butene. [f] May be 1,4-pentadiene. [g] Unknown. [h] Absent or at trace level in reactions carried out at higher power levels or in reaction cells which were not aged. [i] Probably 1,8-nonadiene.
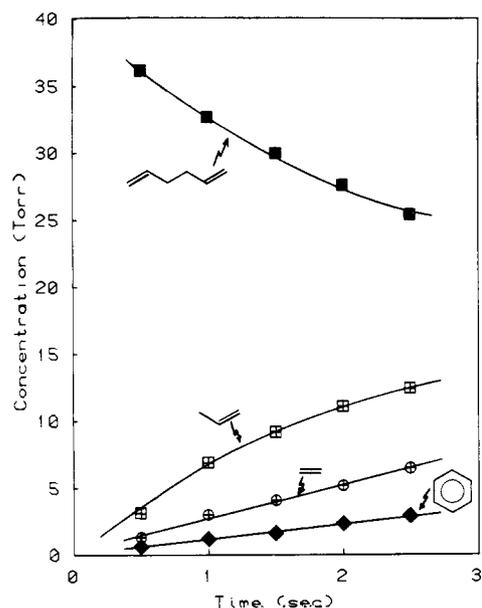
Figure 3. Plot showing the change in concentration with time of 1,5-hexadiene, propene, ethene, and benzene upon irradiation of a sample of 1,5-hexadiene, initially 40 torr, for various times at a laser power of 100 W/cm^2.

propene, ethene, and benzene was constructed, Figure 1. One can deduce that a threshold value of ca. 40 W/cm^2 is required to initiate a reaction at this initial concentration. Above that value the reaction rate increases rapidly with an increase in laser power. Figure 2 is a plot of laser power vs. concentration of propene, benzene, and ethyne from a series of experiments starting with an initial 1,5-hexadiene concentration of 80 torr. When compared to Figure 1, this reveals the concentration dependence of the reaction, as reaction at the higher pressure is well underway at 40 W/cm^2 laser power. This is consistent with a bimolecular process as is suggested by eq 2.

Figure 3 shows the relationship of the concentration of 1,5-hexadiene or the products ethene, propene, and benzene with reaction time. Assuming that the temperature is constant over the different reaction times, these data allow determination of a rate order. These data are best fitted to a $^3/_2$-order rate equation,

Scheme I
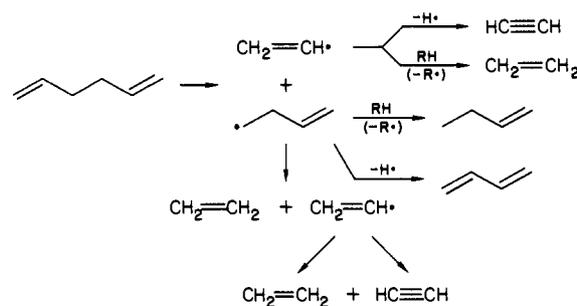
the same as found by Nohara and Sakai.[3] This reaction order is totally consistent with eq 1 and 2 as the rate-determining processes for 1,5-hexadiene disappearance.

At relatively low pressures in a reaction cell with as large a diameter as the one used in this study, the temperature may vary considerably from one location to another. Molecules in the beam may experience temperatures much higher than the average. Nevertheless, an average temperature is useful for comparisons with previous studies. Thus, using Nohara and Sakai's experimental activation energy[3] and our measured rate (based on Figure 3), we can calculate that the average temperature in our reaction cell is 580 °C. On this basis our temperature is comparable to temperatures used in other pyrolytic studies.

The main products observed from the laser-driven reaction (Table I) are also similar to those reported for the static process.[3] Ethyne, 1,2-propadiene, and propyne, however, have not been previously reported from 1,5-hexadiene pyrolysis studies. Like propene, eq 2, propyne and propadiene most likly result from allyl radicals,[22] eq 9. While other routes have been proposed for
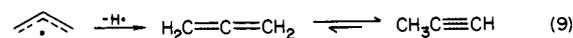
formation of the smaller fragments,[1,2,9] the most economical way to account for several of them is by fragmentation of 1,5-hexadiene between C_2 and C_3, Scheme I, as an alternate path to the major fragmentation (eq 1). At these temperatures (>500 °C), many 1,5-hexadiene molecules may have excess vibrational energy. Hence, they are chemically activated for alternate higher energy

(22) Pola, J. *J. Chem. Soc., Perkin Trans. 2* **1983**, 231.

Table II. Products of Reaction of Hexadienyl Bromides and Chlorides in the Gas Phase and Solution

substrate structure	reaction conditions	product yields (%)										
		low MW components			∿∿	∿∿	∿∿	⬠	⬡	⬡	⬡	other
		C$_2$	C$_3$	C$_4$								
5–7	CW CO$_2$, 100 W/cm^2, 20 s, 5 torr	28.9	7.9	17.6	3.6	14.1	1.3		4.9	14.6	5.4	1.7
2–4	CW CO$_2$, 75 W/cm^2, 20 s, 14 torr	6.3 (C$_2$+C$_3$)		4.5	5.6	3.1	2.3			73.4	4.5	
5–7	soln in Ph$_2$O, AIBN, (Bu)$_3$SnH, 4 h, 100 °C				17.9	42.7		37.3	<0.1			

Scheme II
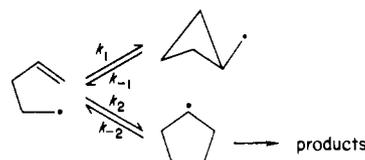
reaction pathways.[23-26] However, results discussed below suggest that the C$_2$ and C$_4$ products most likely come from radical **1**.[9]

Cyclization Mechanisms. Evidence from other studies[6,25-27] suggests that allyl radicals may react with ethene and with ethyne to directly form the cyclic C$_5$ products observed here. For example, Nohara and Sakai[27] found that cyclopentadiene amounted to greater than 90% of the C$_5$ products when allyl radicals reacted with ethyne under conditions similar to those used in their 1,5-hexadiene pyrolysis studies. In the reaction of ethene and allyl radicals, cyclopentene was the major C$_5$ product, but a substantial amount of 1-pentene was also present.[6,25] The suggested mechanism for formation of cyclopentene[25] is stepwise addition to form the 4-penten-1-yl radical with cyclization leading to the cyclopentyl radical; hydrogen atom loss completes the sequence. The suggested radical cyclization is unknown in solution and, as written, gives the wrong regioisomer based on experimental and theoretical knowledge.[10,28,29] Beckwith[10] has estimated that the 4-penten-1-yl radical would go 100% to the cyclobutylmethyl radical (exo mode) rather than to the cyclopentyl radical (endo mode). However, attempts to observe this in solution have led to noncyclic products.[10,24]

Sakai and Nohara[25] rationalized their gas-phase products by suggesting that the 4-penten-1-yl radical had excess vibrational energy (chemical activation[23-26]). Watkins and Olsen[26] have also discussed the apparently abnormal gas-phase regioselectivity of the 4-penten-1-yl radical cyclization using the same argument. Recent experiments of Beckwith et al.[24] provide a basis for an alternate explanation. They observed that a wide variety of cyclobutylmethyl radicals readily opened to the corresponding 4-penten-1-yl radicals when the former were formed in solution. Even tertiary cyclic radicals were found to readily ring open to primary radicals, eq 10. With this knowledge, we suggest that

$$\tag{10}$$
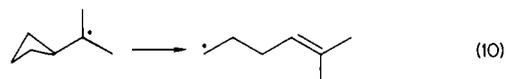
both cyclization modes may be competitively occurring with the exo mode being greatly preferred (>99%). However, the cyclic radical formed by exo mode cyclization is kinetically unstable and readily reverts to the open-chain radical. The endo mode occurs much more slowly but produces a kinetically stable cyclic radical.[10] The situation is shown in Scheme II. Since we anticipate that $k_1 \gg k_2$, $k_{-1} \simeq k_1$, and $k_{-1} \gg k_{-2}$, in the gas phase, only products from the favored process may result (thermodynamic control).

Accounting for the six-membered-ring products is complicated by the fact that a non-radical cyclization pathway, i.e., eq 6, may compete with a radical pathway, i.e., eq 3, as mentioned earlier. To ascertain if these processes compete, we explored the alternate pathways. By irradiation of a mixture of (E)- and (Z)-1,3,5-hexatriene under conditions similar to laser-induced experiments with 1,5-hexadiene, we found that the *cis*-triene was totally converted to 1,3-cyclohexadiene and the *trans*-triene was rapidly converted apparently to the *cis*-triene and then to 1,3-cyclohexadiene. In a typical experiment, a triene mixture (20 torr), initially 55% trans, was irradiated at 100 W/cm^2 for 5 s, giving (by GC analysis) 1,3-cyclohexadiene (83.4%) and *trans*-1,3,5-

(23) Chang, M. H.; Jain, R.; Dougherty D. A. *J. Am. Chem. Soc.* **1984,** *106,* 4211.
(24) Shen, K. K.; Bergman, R. G. *J. Am. Chem. Soc.* **1977,** *99,* 1655.
(25) Sakai, T.; Nohara, D. *Bull. Jpn. Pet. Inst.* **1975,** *17,* 212.
(26) Watkins, K. W.; Olsen, D. K. *J. Phys. Chem.* **1972,** *76,* 1089.
(27) Nohara, D.; Sakai, T. *Ind. Eng. Chem. Fundam.* **1980,** *19,* 340.
(28) Beckwith, A. L. J.; Moad, G. *J. Chem. Soc., Perkin Trans. 2* **1980,** 1083.
(29) Bischof, P. *Tetrahedron Lett.* **1979,** 1291.

hexatriene (15.5%). The only other components present in the chromatogram were several minor peaks (total = 1.1%) just above the noise level. As no benzene was formed, radicals are absent since Benson and Shaw found that 1,3-cyclohexadiene readily forms benzene in the presence of radicals.[30] The results of this experiment are consistent with the reactions shown in eq 6 and 7.[7,8]

To determine the course of reaction of radical **1**, the mixture of chloride precursors **2–4** (14 torr) was irradiated in the gas cell for a time sufficient to convert 83% of reactants to products. GC analysis of the products revealed the mixture shown in Table II. The unreacted starting material was found to have a composition (**2:3:4** = 72:16:12) similar to the starting composition (**2:3:4** = 83:10:7). Therefore, each isomer was converted to product with **2** being slightly more reactive than **3** and **4** as expected. Chlorine was present in the product mixture as HCl (by IR analysis). While concerted elimination of HCl may account for most of the 1,3,5-hexatriene (vide infra),[31] radical **1** is undoubtedly formed as evidenced by the presence of products which require radical precursors: 1,4-hexadiene, 1,5-hexadiene, benzene, propene, etc. Thus at least a part of the 1,3-cyclohexadiene must have come from radical **1**. Because *trans*-1,3,5-hexatriene is an observed product, eq 5–7 are occurring to some extent. Unfortunately, no product is formed which *must* be accounted for by invoking a radical cyclization pathway. All of the cyclic products *could* arise via eq 6 and 7.

2, X = Cl
5, X = Br

3, X = Cl
6, X = Br

4, X = Cl
7, X = Br
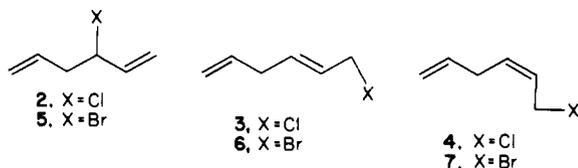
Since a weaker C–X bond favors formation of **1**, the bromo-hexatriene isomers **5–7** were subjected to laser photolysis, Table II. Indeed from the products formed, there is substantial evidence that the yield of radical **1** was higher from the bromide precursors. First, the yield of 1,3-cyclohexadiene is substantially reduced, indicating a lowered yield of the concerted HX elimination pathway.[31] Also, the production of greater quantities of C_2, C_3, and C_4 products is evidence of the intermediacy of **1**. James and Troughton[9] suggested that **1** is a primary source of 1-butene, 1,3-butadiene, ethene, and ethyne. Perhaps the most significant indicator of the presence of radical **1**, and for its cyclization, is the presence in this reaction of 1,4-cyclohexadiene. Although 1,4-cyclohexadiene is known to give benzene by concerted loss of H_2,[30] we found that 1,4-cyclohexadiene is not totally converted under our reaction conditions. 1,4-cyclohexadiene is best accounted for by invoking cyclization of **1** to the six-membered ring, eq 3, followed by loss of a H radical from the cyclic radical to give 1,4-cyclohexadiene (along with the favored 1,3-diene, eq 4).

To assess the ring-size preference in the cyclization of radical **1**, we turned to the solution procedure used by other workers for

such studies.[10,32] With use of the isomeric bromohexatriene isomer **5–7**, the radical reaction to produce **1** was carried out and the products were determined by GC, Table II. The noncyclic products were high in this reaction not only because the solution was reasonably concentrated but because radical **1** has both cis and trans configurations.[33] Nevertheless, cyclohexene, the product anticipated from cyclization of **1** to a six-membered ring, was below the detectable limit (0.1%). Therefore, the five-membered-ring product, formed in 37% yield, is highly favored kinetically.

In light of the above solution results, we must account for the lack of products derived from the cyclopentenylmethyl radical (e.g., 4-methylcyclopentene) or assume that the radical cyclization pathway is not occurring in the gas phase. We believe the argument developed above to explain the regioselectivity of cyclization of the 4-penten-1-yl radical also applies in this instance. Thus, in the gas-phase pyrolysis of 1,5-hexadiene, radical **1** is an intermediate which reacts by competing pathways. Our evidence indicates that some portion of **1** is converted into the 1,3,5-hexatrienes (eq 5). However, radical cyclization also occurs by eq 3 and 8. The cyclopentenylmethyl radical, which forms faster than the corresponding six-membered-ring cyclization product, is kinetically unstable and reverts to **1**. Thus, only the six-membered rings survive. In addition to the precedents mentioned above, Gordon and Smith found that cyclohexyl radicals ring-open in the gas phase above 300 °C to give the open-chain radical which cyclizes in part to methylcyclopentane.[34] Methylcyclopentane, however, is not among the products above 420 °C.[34] Since it is known that, at least for small rings, the radical formed from exo mode cyclization is less stable than the isomeric radical from endo mode cyclization,[10] at high temperatures thermodynamic control is observed. Hence, the endo mode product results.

Finally, we must comment on the differences between the gas-phase and solution products. Lamb et al. were the first to comment of the differences on comparing their solution reactions of the 5-hexen-1-yl radical with the results of Gordon and Smith.[34,35] There are a number of obvious differences such as the solvent which provides such a dominant quenching reaction. This is critically important when the reversibility of the cyclization reactions is considered.

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(33) On the basis of experimental and theoretical treatments of simpler radicals, there should be about a kcal/mol difference in the energy of the (*E*) and (*Z*) forms of **1** and about a 10–15 kcal/mol barrier to isomerization, cf.: Schleyer, P. v. R.; Dill, J. D.; Pople, J. A.; Hehre, W. J. *Tetrahedron* **1977**, *33*, 2497. Montague, D. C. *Int. J. Chem. Kinet.* **1973**, *5*, 513. Gorton, P. J.; Walsh, R. *Chem. Commun.* **1972**, 783. Golden, D. M.; Gac, N. A.; Benson, S. W. *J. Am. Chem. Soc.* **1969**, *91*, 2137.
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