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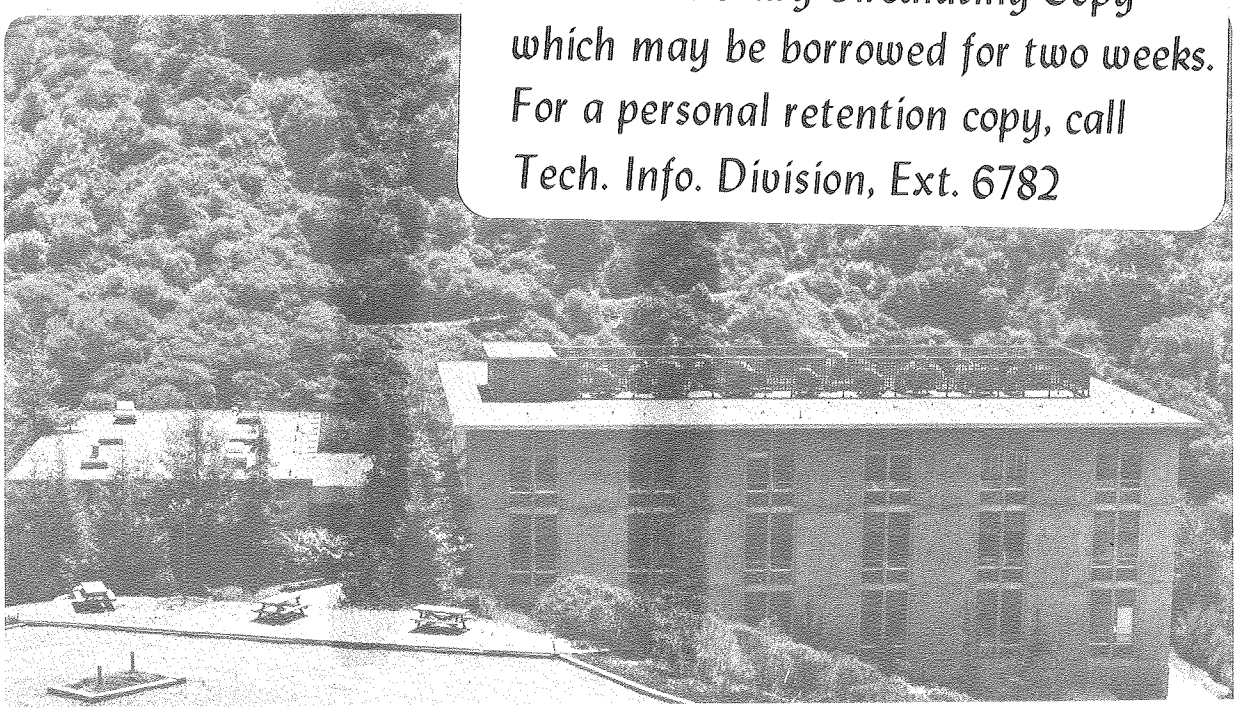

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LASER-POWERED HOMOGENEOUS DISSOCIATION OF TETRALIN

By Paul B. Comita, Michael R. Berman, C. Bradley Moore, and Robert G. Bergman

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Abstract. In an effort to determine the products and mechanism of the truly homogeneous thermal dissociation of the aromatic hydrocarbon tetralin, we have examined the products formed from this compound upon energization by infrared multiphoton excitation and SiF_4-sensitized infrared thermal activation. Six major products are formed in these reactions, three of which appear to be primary dissociation products: these three are benzocyclobutene, o-allyltoluene, and 1,2-dihydronaphthalene. The lowest energy reaction channel is the ethylene-loss channel resulting in benzocyclobutene. The ring cleavage channel, giving rise to o-allyltoluene, has not been previously observed. The dehydrogenation reaction, which forms 1,2-dihydronaphthalene, results primarily in loss of hydrogen from C1 and C2 and is predominantly a non-concerted hydrogen elimination. We believe that in previous studies, where dehydrogenation was reported as the primary dissociation channel, the experiments were complicated by surface catalysis. In the laser-induced reactions, which are uncomplicated by problems due to surface catalysis, the true homogeneous decomposition takes place, and this involves primarily ethylene loss.

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INTRODUCTION

The recent literature contains a number of investigations describing the thermal reactions of tetralin (1; structure illustrated in Fig. 1), primarily directed toward an understanding of the fate of 1 when it is thermalized in the presence of coal[1]. Several investigators have undertaken gas phase pyrolyses in the absence of coal in order to determine the true unimolecular thermal reactivity of 1. For example, Gangwer et al.[1e] found that when 1 was pyrolyzed in the gas phase in a static quartz reactor, the dehydrogenation of 1 followed zero order kinetics. They also found a rate dependence on vessel surface history. In an earlier investigation, Loudon et al.[1a] reported product distributions resulting from static pyrolyses which were completely different from those reported by Gangwer. Products resulting from loss of carbon-containing fragments were found, but yields of benzocyclobutene (2), a product which might be expected from a retro-(2+4) reaction, were always present in less than 2%.

Our reinvestigation of the thermal reactivity of 1[2] was prompted by our observation that highly energized 1 produced by chemical activation of 1 resulted primarily in ethylene loss, giving rise to 2.[3] This raised the possibility that the true homogeneous thermal reactivity of tetralin was being masked by surface catalysis of the dehydrogenation reaction channels in the normal thermal activation experiments. A method of energization not mediated by hot, potentially catalytic surfaces was therefore required. Two techniques were employed here, both utilizing a TEA CO_2 laser as the source of excitation. These were infrared multiphoton dissociation (MPD) and SiF_4-sensitized thermal activation. In MPD experiments, laser energy is deposited in the vibrational modes of 1, providing direct excitation. When low laser

fluence is used and the up-pumping rate does not greatly exceed the dissociation rate, dissociation primarily occurs through the lowest energy reaction channel.[4] When the up-pumping rate is increased, higher energy channels become accessible.

Sensitized thermal activation employs a non-reacting gas to absorb the laser energy. SiF_4 is an ideal sensitizer due to its strong absorbance in the CO_2 laser radiation region and large bond dissociation energy.[5] In the sensitized experiments, molecules of 1 in the volume irradiated by the laser beam are thermally excited by collisional energy transfer from the sensitizing gas.[6a] The temperature achieved is altered by varying the incident laser intensity or the gas mixture in the cell.

We report here our investigations directed toward an understanding of the true homogeneous thermal reactivity of tetralin. The experiments utilize CO_2 laser activation as a means of avoiding surface catalytic reactivity. Three primary reaction products are observed: these are benzocyclobutene, o-allyltoluene (4), and 1,2-dihydronaphthalene (6). Mechanistic details of tetralin's reaction channels are investigated using tetralin appropriately labeled with deuterium.

EXPERIMENTAL

Photolysis

A schematic diagram of the experimental arrangement for the SiF_4-sensitized photolyses is shown in Figure 2. The laser was a grating-tuned TEA CO_2 laser (Tachisto Model 215) equipped with a Ge output coupler coated for 50% reflectivity on the inner surface and anti-reflection coated on the output side. Photolyses of 1-d_{10} and the mixed isotope experiments were

performed with the laser internal iris set at 0.8 cm. All other experiments used a 1.2 cm internal iris with a 0.7 cm external iris to define the incident beam size. The former technique generated a much more reproducible, well-defined Gaussian beam. The CO_2 laser was operated on the P(40) line at 1027.4 cm^{-1}. The unattenuated laser output was about 0.27 J/pulse in a 0.7 cm diameter beam. Attenuation was performed with a gas cell filled with 0 to 10 Torr of SiF_4. The laser beam was not focused. The incident energies used ranged from 0.11 to 0.27 J/pulse. The maximum fluence and power density were 0.7 J/cm^2 and 3.5 MW/cm^2 respectively.

A small portion of the laser energy (10%) was directed into a Scientech (model 36-0001) power meter (PM 1) by a 4mm thick polished NaCl flat (BS). The readings from PM 1, denoted throughout by the superscript BS, were used as measurement of the laser power in order to normalize the total energy reaching PM2 (Scientech model 38-0101). The output from each power meter was recorded on a dual pen chart recorder (Leeds and Northrup) throughout the photolysis. Prior to each photolysis, I_o, the energy reaching PM2 with no cell in the beam path, and I_o^{BS} were measured.

During SiF_4-sensitized photolysis, the laser beam passed through the center of the photolysis cell and irradiation continued until the desired conversion of starting material, between 1 and 10%, was achieved. This typically required between 200 and 2000 pulses, depending on the laser intensity and the gas mixture in the cell. The incident energy (PM 1), I_t^{BS}, and the energy transmitted through the cell (PM 2), I_t, were monitored throughout the photolysis. The average laser power was maintained constant to within ±5% during the course of a photolysis and pulse-to-pulse variations were less than ±10%. Photolyses were performed at a laser repetition rate of either 1.00 or 0.87 Hz.

After a photolysis, the laser beam was blocked from the photolysis cell and the condensible materials in the cell frozen into the sidearm with liquid N_2 (LN_2). Care was taken not to touch the cell or close the stopcock during this process so the empty cell transmission, I_c, could be measured with the cell in the exact position as it was during the photolysis. Finally, the photolysis cell was removed and the incident laser power and the beam splitter calibration measured.

MPD experiments were performed with an arrangement similar to that shown in Figure 1 except that the beam splitter (BS) is replaced by a 15 cm focal length NaCl lens. The focal point was approximately at the center of the cell. Photolyses were performed at 946.0cm^{-1}. The laser beam was attenuated with an SF_6 gas cell (10cm long, 10-25 torr SF_6).

Sample Handling

The low vapor pressure of I at 295K (0.4 torr), its solubility in hydrocarbon greases and its penchant for sticking to surfaces dictated many of the experimental conditions and procedures employed. Extreme care was taken to avoid contamination of the starting materials and products from molecules desorbing from the walls of the vacuum system. A glass vacuum system with greaseless stopcocks (Kontes 4mm) and a base pressure of 10^{-6} torr was used. No hydrocarbon greases were used. O-ring joints, silicone grease (Dow-Corning 970V) or black wax were used where needed. The vacuum manifold was warmed with heating tape to 80°C or higher when not being used to expedite desorption from the walls. Two LN_2 cooled traps were used, one directly after the diffusion pump and the other adjacent to the manifold. The latter significantly helped in preventing contamination of samples or

products that were vacuum transferred through the manifold. Since SiF_4 reacts rapidly with water to produce HF, all surfaces which came in contact with SiF_4 were heated under vacuum to remove adsorbed water. The vacuum line manifold was removed, cleaned in Chromerge solution, and baked out between series of experiments which involved different tetralin isotopomers. Pressures were measured with a capacitance manometer (MKS Baratron Type 222 AHS).

MPD experiments were carried out in a cell consisting of a 2cm i.d. by a 20cm long Pyrex cell with KCl windows mounted at the Brewster angle. Sensitized photolyses were performed with 4.0cm i.d. pyrex cells. The cells were either 3.85 or 4.00cm long, with the exception of a 1.0cm long cell used for studying the effect of cell surface area on the photolysis. All cells had two polished NaCl or KCl windows affixed parallel to one another with epoxy (Eccobond 45). Different cells were employed for each tetralin isotopomer used. A similar 4.00 cm long cell, equipped with 2.0 cm diameter NaCl windows above and below the laser beam, was used for viewing infrared fluorescence.

The sample handling procedure for sensitized photolysis experiments was as follows: SiF_4 was expanded into the cell (between 5 and 10 torr), frozen into the sidearm with LN_2, and the stopcock to the sidearm closed. The cell was then pumped out and 1 (usually 0.325 torr) was expanded into the cell. The sidearm was then warmed and opened to allow the SiF_4 to expand into the cell. Five minutes were allowed for equilibration of the gases before photolysis was initiated. If the procedure was reversed and 1 frozen into the sidearm, equilibration of 1 into the gas phase would require inordinate amounts of time, and droplets of 1 could be seen in the sidearm. Residual 1 in the main manifold was not frozen into the sample reservoir

after loading a cell, to prevent contamination of the starting material. Some photolysis cells had an additional sidearm containing a reservoir of 1 so that cells could be filled directly, eliminating unnecessary contact with the vacuum manifold. Gases and all hydrocarbon reactants were degassed by repeated freeze-pump-thaw cycles prior to use.

After equilibration of the gases, the gas mixture was photolyzed. Condensible materials were frozen into the sidearm with LN_2 following the photolysis. When non-condensible products were analyzed, they were either directy injected into a mass spectrometer or sampled for analysis by gas chromatography (GC) with a gas syringe (Precision Sampling No. 010033) through a septum placed over the cell outlet joint. The volume between the septum and the cell was flushed with N_2. The sidearm was then warmed with a dry-ice-isopropanol bath (195 K). SiF_4 and other gases were either pumped away or collected with LN_2 for GC analysis. The remaining contents of the cell were transferred to the collection tube containing 20 μl of n-hexane solvent. The collection tube consisted of a 5 cm piece of 2 mm i.d. Pyrex glass tubing blown onto a 14/20 outer standard taper joint. When several tetralin isotopomers were used simultaneously on the vacuum line, individual transfer manifolds were used to vacuum transfer materials from the cell to the collection tube.

Analysis

The solutions of photolysis products were usually analyzed by GC or coupled GC-mass spectroscopy (GC-MS), An internal standard, 1.0 μl of n-undecane solution in n-hexane (0.018 or 0.058M), was added to the solution with a syringe before GC analysis. Samples for GC analysis were taken from the collection tube with a syringe by two techniques: 1) via a Teflon

Mininert valve, 2) via a septum placed on the collection tube. If the sample was stored prior to analysis, the 2mm tubing was sealed off with a torch with the contents frozen in the bottom of the tube at 77 K. The glass seal was broken and the sample solution was exposed to the atmosphere when sampled by a syringe. These sampling techniques were used interchangeably. The quantitative nature of the entire collection and sampling technique was checked by transferring and analyzing standards of 1, 3, and 5.

The sample handling for SiF_4-sensitized photolyses of benzocyclobutene (2), o-allyltoluene (4), and 1,2-dihydronaphthalene (6) were as described above. Sample handling for MPD experiments was similar with the omission of the SiF_4 steps.

GC analyses were performed on a Perkin-Elmer Sigma 3 gas chromatograph equipped with a 250 ft by 1/16 in o.d. stainless steel OV-17 wall coated open tubular (WCOT) column and flame ionization detectors. The column temperature was programmed as follows: 110°C, 12 min.; 110-120°C, 5 min; 120°C, 35 min. Injections of 0.06 μl were made with a 1 μl syringe (Hamilton #7101) into an injector port heated to 175°C. The He carrier gas flow rate was 10 mL/min. Digital integration of the GC peaks was accomplished with a Spectra-Physics Autolab System I Computing Integrator interfaced to the GC. At least two injections of each sample were made and the product signals relative to either the tetralin or internal standard signals agreed from injection to injection to within ±3%. Results from the repetition of an experiment agreed to within ±5%. The integrations were corrected for the FID response of each compound. GC analysis of gaseous products were performed with a 10 ft by 1/8 in o.d. stainless steel Porapak T (100/120 mesh) column.

Isotopic analysis was achieved by GC-MS analysis on a Finnegan 4000

GC-mass spectrometer. All GC-MS analysis was performed with a 30m glass capillary SP-2250 WCOT column and an electron energy of 20 eV to limit fragmentation. Mass spectral analyses of gaseous products were performed on an AEI-MS 12 mass spectrometer at 20 eV . The responses of H_2 and D_2 were calibrated with known samples of H_2 and D_2.

Infrared spectra of 1 with $1cm^{-1}$ resolution were recorded with a Nicolet Model 7199 FTIR. Spectra were taken of a thin film of 1 between two NaCl plates and 1 in the gas phase in a multiple pass cell (Wilks 20M) using a path length of 9.75m.

Infrared fluorescence from SiF_4 was observed using a liquid helium cooled Cu:Ge detector. Fluorescence was observed in the 2000 cm^{-1} region through an interference filter (OCLI W4741-4) with a peak transmission of 88% at 2110 cm^{-1} and 10% power points at 1850 and 2430 cm^{-1}. Fluorescence was collected with a 5.0cm f/1 CaF_2 lens. In order to observe fluorescence at all frequencies above 700 cm^{-1}, the CaF_2 lens was replaced by a 5.0 cm f/1 NaCl lens. All CaF_2 and MgF_2 windows were removed from in front of the detector and replaced by a 4.0cm long cell with NaCl windows containing 200 Torr SiF_4. Scattered light was still very large. Signal averaging was performed with a Tracor-Northern NS 575 A and a Biomation 8100 transient digitizer.

Materials

General

^{1}H-NMR spectra were obtained on an EM-390, UCB-180 (a superconducting 180 MHz FT instrument), or UCB-250 (a superconducting 250 MHz FT

instrument) spectrometer. Chemical shifts are expressed in ppm downfield from tetramethylsilane (TMS). ^{2}H-NMR spectra were obtained on the UCB-180 spectrometer at 27.64 MHz.

High resolution mass spectra (HRMS) were obtained on a Dupont CEC21-110B spectrometer. Low resolution MS were obtained on an AEI-MS12. Infrared spectra were recorded on a Perkin-Elmer Model 237 grating spectrophotometer. Elemental analyses were performed by the Microanalytical Laboratory operated by the College of Chemistry, University of California, Berkeley, California.

Preparative GC was performed on either a Varian 90P or 920 instrument equipped with a thermocouple detector. The GC columns used in this work were the following: Column A: 15 ft. X 3/8 in. stainless steel 20% OV-17 on 60/80 Chrom P-AW/DMCS; Column B: 5 ft. X 1/4 in. silanized glass column with 10% SF-96 on 60/80 Chrom W-AW/DMCS.

Gases

SiF_4 was obtained from Matheson Co., Inc. and was purified by trap-to-trap distillation from -131 to -196°C. D_2 (99.6% D, CP grade) and H_2 were obtained from Matheson Co., and were used without purification.

Identification of Products

All six major products from the thermolysis of 1 were identified by comparison of ^{1}H-NMR spectra, IR spectra, mass spectra, and GC retention time with those of authentic materials. These were benzocyclobutene (2), styrene (3), o-allyltoluene (4), indene (5), 1,2-dihydronaphthalene (6), and naphthalene (7, see Figure 1). A large scale pyrolysis of tetralin afforded

a mixture of products which were isolated by preparative GC on Column A. Authentic samples of 3, 5, 6, and 7 were available from commercial sources. Authentic samples of 2 and 4 were obtained by independent syntheses (see Syntheses section).

Syntheses

o-Allyltoluene. This compound was prepared in 69% yield by the method of Hurd and Bollman[7], and was purified by preparative GC on Column A. ^{1}H-NMR (CCl_4): δ= 2.20 (s, 3H), 3.24 (doublet of triplets, 2H, J_d- 6.0, J_t- 1.8), 4.79 (doublet of quartets, 1H, J_d-11.3, J_q-2.1), 4.93 (multiplet, 1H), 5.79 (quartet of triplets, 1H, J_q-11.3, J_t-6.5), 6.94 (singlet, 4H). MS (50 eV): m/e 132 (parent), 117 (base).

Benzocyclobutene. This compound was prepared in 50% yield by the method of Schiess et al.[8], and was obtained free from styrene by preparative GC on Column B. ^{1}H-NMR ($CDCl_3$): δ= 3.11 (s, 4H), 7.01 (multiplet, 4H). MS (50 eV): m/e 104 (parent, 100% relative abundance (RA)), 103 (53% RA), 78 (59% RA), 51 (52% RA).

1,2,3,4-tetrahydro-1,4-d_2-naphthalene-1,4-d_2 (1-d_4). To 11.55mL of a solution of 2.60M $NaCD_2SOCD_3$ in DMSO-d_6, prepared by the method of Corey et al.[9], was added 1 (1.00g, 7.58mmol) via syringe. This mixture was allowed to stir and was monitored conveniently by ^{1}H-NMR. After 48 hours the reaction was quenched with 600µL of D_2O. Petroleum ether (20mL) was then added and the mixture was extracted with two 10mL portions of H_2O. The organic layer was filtered and dried with $MgSO_4$. The solvent was removed under reduced pressure to yield 0.62g (60% yield) of crude tetralin with deuterium in the benzylic positions. This procedure was repeated until 1-d_4 was obtained

containing 98.7% D-incorporation as judged by MS analysis. ^{1}H-NMR (CCl_4): δ= 1.77 (s, 4H), 6.88 (s, 4H). IR (thin film): 3100-2840, 2220-2060,1455,1495, 787,728 cm^{-1}. MS (10 eV): m/e 137 (11.1% RA), 136 (parent, 100% RA), 135 (6.7% RA). MS (50 eV): m/e 136 (81% RA), 108 (93% RA), 107 (67% RA), 106 (base, 100% RA), 94 (44% RA).

<u>1,2,3,4-tetrahydro-1,2,3,4-d_4-naphthalene-d_8</u> (1-d_{12}). A stainless steel bomb was charged with naphthalene-d_8 (1.95g, 14.3mmol, Aldrich Chem. Co., 98+ atom% D), 5% Pd on carbon (309.5mg, 0.14mmol Pd), and 50mL CH_3OD (Aldrich Chem. Co., 99.5+ atom% D). The bomb was connected to a high-pressure stainless steel manifold and was evacuated with a rough pump and flushed with D_2 twice. The bomb was then pressured to 750 psi D_2 and heated to 60°C with stirring. After 18 hours, the bomb was recharged to 750 psi and then allowed to stir for another 24 hours. The contents of the bomb were gravity filtered and the solvent was removed under reduced pressure to yield 1.43g 1-d_{12} (69.2 % yield). Analytical GC showed the product to be 99.3% tetralin and 0.7% decalins. Analytically pure material was obtained by preparative GC on Column A. ^{2}H-NMR (benzene-h_6): δ=1.80 (s, 4D), 2.84 (s, 4D), 7.3-7.7 (broad singlets, 4D). IR (thin film): 2260, 2190, 2100, 1399 cm^{-1}. MS (17 eV): m/e 145 (11% RA), 144 (parent, 100% RA), 143 (22.0% RA). HRMS: Calcd. for $C_{10}D_{12}$: 144.1692; found, 144.1688. Elemental analysis: Calcd. for $C_{10}D_{12}$: C, 83.25%; D, 16.75%. Found: C, 83.32%; D, 16.92%.

<u>1,2-dihydro-1,2-d_2-naphthalene-d_8</u> (6-d_{10}). A dry 25mL one-neck round-bottom flask was charged with 1-d_{12} (1.0g, 69.4mmol), N-bromosuccinimide (1.36g, 76.4mmol, recrystallized from H_2O), AIBN (3.7mg) and dry CCl_4 (10mL). The flask was fitted with a reflux condenser and flushed with dry N_2. After refluxing for two hours the mixture was diluted with 40mL CCl_4 and then extracted with five 20mL portions of hot H_2O. The CCl_4 layer

was then dried with Na_2SO_4. The solvent was removed under reduced pressure to yield 1.18g of a mixture of 1-d_{12}, 1-bromotetralin-d_{11}, and di-brominated tetralin-d_{10}. Column chromatography on a 17.5in X 1in o.d. SiO_2 column with 1% benzene in hexanes gave rise to clean dehydrohalogenation to yield 1-d_{12}, 6-d_{10}, and naphthalene-d_8. The fractions containing 6-d_{10} were combined and the solvent removed under reduced pressure to yield 0.422g (43% overall yield) of 6-d_{10}. Analytically pure material was prepared by GC on Column A. ^{2}H-NMR (benzene-h_6): δ=2.26 (s, 2D), 2.80 (s, 2D), 6.10 (s, 1D), 6.68 (s, 1D), 7.24-7.35 (overlapping singlets, D). IR (thin film): 2280, 2205, 2100 cm^{-1}. HRMS: Calcd. for $C_{10}D_{10}$: 140.1410 ; found, 140.1406. Elemental analysis: Calcd. for $C_{10}D_{10}$: C, 85.63%; D, 14.37%. Found; C, 85.77%; D, 14.66%.

<u>cis-1,2,3,4-tetrahydro-1,2-d_2-naphthalene-d_8</u> (<u>cis</u>-1-d_{10}). A Parr hydrogenation flask was charged with 6-d_{10} (200mg, 1.43mmol), PtO_2 (2.8mg, 0.012mmol), and 20mL MeOH. The Parr hydrogenator was pressured to 50 psi with H_2 and the mixture allowed to react for 30 min. The MeOH was removed under reduced pressure to yield 192mg (94% yield) of <u>cis</u>-1-d_{10}. The compound was prepared analytically pure by preparative GC on Column A. ^{1}H-NMR ($CDCl_3$, D-decoupled): δ= 1.74 (d, 1H, J_{12}=5.4), 2.72 (d, 1H, J_{12}=5.4). D-NMR (benzene-h_6): δ=1.76(s, 3D), 2.75 (s, 3D), 7.28 (2 overlapping singlets, 4D). IR (thin film): 2928, 2270, 2200, 2109, 1520, 1408 cm^{-1}. HRMS: Calcd. for $C_{10}H_2D_{10}$: 142.1567; found, 142.1565. Elemental analysis: Calcd. for $C_{10}H_2D_{10}$: C, 84.43%; H+D, 15.57%. Found; C, 84.83%; H+D, 15.69%.

<u>1,2,3,4-tetrahydro-1,3,4-d_3-1-naphthalen-2,3,4,5,6,7,8-d_7-ol</u> (14). A solution of 6-d_{10} (1.24g, 8.84mmol) in 10mL THF was cooled to 0°C under N_2 in a dry 25mL 3-neck flask. BH_3-THF complex (5.78mL, 1M solution, Aldrich Chem. Co.) was added via syringe using a syringe pump for 1/2 hr. The mixture

was quenched with 0.6mL H_2O, stirred for 15 min., and then cooled to 0°C. A solution of 3M NaOH (1.9mL) was added at once and subsequently a 20% H_2O_2 solution (1.27mL) was added while keeping the temperature below 40°C. The mixture was allowed to reflux for one hour at 50°C and then stirred overnight. NaCl was then added and the mixture was extracted with 4X5mL THF. The THF layer was dried with $MgSO_4$, filtered, and the solvent was removed under reduced pressure. After column chromatography on silica gel with 15% v/v Et_2O/benzene solvent, the pure deuterated tetralol (1.20g, 86% yield) was obtained. ^{1}H-NMR ($CDCl_3$): δ=1.80 (broad singlet, 1H), 1.70 (s, 1H). IR (thin film): 3350, 2900-2960, 2100-2300cm^{-1}. MS (15eV): m/e 158 (44% RA, parent), 140 (100% RA), 139 (79% RA). Elemental analysis: Calcd. for $C_{10}H_2D_{10}O$: C, 75.88%; H+D, 14.01%. Found: C, 75.46%; H+D, 14.17%.

<u>cis- and trans-1,2,3,4-tetrahydro-1,2-d_2-naphthalene-d_8</u> (<u>cis</u>- and <u>trans</u>-1-d_{10}). A solution of 14 (200mg, 1.26mmol) and triphenylphosphine (418mg, 1.59mmol) in 0.60mL dry CCl_4 was allowed to reflux for 60 hours at 90°C. The mixture was cooled to 0°C and the solids were filtered. The filtrate solvent was removed under reduced pressure and the oil was taken up in petroleum ether. The resulting solids were filtered and the solvent was removed under reduced pressure. The resulting crude 1-Cl-1,2,3,4-tetrahydro-1,3,4-d_3-naphthalene-d_8 (180mg, 80.6% yield) could not be purified by column chromatography or preparative GC without dehydrochlorination. A solution of this oil (154mg, 0.974mmol), tri-n-butyltin hydride (262µl, 0.993mmol), and several crystals of AIBN in 0.60mL ethanol (dry) was allowed to reflux at 80°C overnight. A mixture of cis- and trans-1-d_{10} was obtained (82% yield, 66% overall yield) with spectroscopic characteristics identical with that of cis-1-d_{10} with the exception of the 2-D J spectrum (see below in <u>Synthesis of Labeled Tetralin</u>).

Synthesis of Labeled Tetralin

Tetralin-d_4 was obtained by reaction of 1 with $NaCD_2SOCD_3$ in DMSO-d_6. Three successive exchanges were necessary to obtain 1-d_4 with 97.6% deuterium incorporation.

Synthesis of cis-1-d_{10} was accomplished in four steps starting from naphthalene-d_8 (see Figure 3). Proof of stereochemistry in cis-1-d_{10} was accomplished with 2-dimensional ^{1}H-NMR-J-spectroscopy.[10] Heteronuclear couplings are suppressed from the 90° projection of a 2D-J-spectrum, resulting in a J-spectrum symmetrically disposed about zero frequency and separated by the ^{1}H-^{1}H couplings. The cis-1-d_{10} displays a ^{1}H-^{1}H coupling of 5.5 Hz.

In order to confirm that stereochemical scrambling did not take place in the catalytic reaction giving rise to cis-1-d_{10}, a mixture of the cis- and trans-1-d_{10} was synthesized in three steps from 6-d_{10} as depicted in Figure 3. The 90° projection of a 2-D J spectrum of the mixture of cis and trans isomers displayed two overlapping doublets, with one coupling larger than 5.5 Hz (approximately 7.0 Hz), due to the trans isomer.

SENSITIZED PYROLYSIS TECHNIQUE

The sensitized pyrolysis technique has been employed in several systems.[5,6] This technique enables the use of intense lasers to indirectly excite molecules which do not absorb laser radiation. Both pulsed and continuous-wave[6e] CO_2 lasers have been used as excitation sources. Several sensitizing gases, such as SF_6, CH_3F, NH_3, and SiF_4, have been employed[5,6]. SiF_4 is an excellent sensitizer due to its large absorption coefficient in the region of the 9 m CO_2 laser transition and due to the large F_3Si-F bond

dissociation energy. SiF_4 has been found to be unreactive in the presence of organic molecules under pyrolysis conditions similar to those employed here.[5] Tetralin does not absorb significantly at the laser frequency used to excite SiF_4.

The absorption coefficient of SiF_4 increases with increasing SiF_4 pressure between 5 to 10 Torr with the laser intensity ($1 MW/cm^2$) used. The fraction of the incident energy absorbed by SiF_4 increases by about 10% as the laser energy is decreased from 0.2 to 0.1 J/pulse, probably as a result of saturation. These characteristics of SiF_4 absorption have been previously observed.[5] Typically, 25% of the incident energy is absorbed by the SiF_4 in these experiments. Stronger absorption is undesirable in order to limit the non-uniformity of the distribution of the absorbed energy along the length of the cell.

In order to investigate the competition between reaction channels of tetralin decomposition as a function of the temperature in SiF_4-sensitized pyrolyses, a means for determining the quantity of energy absorbed per pulse is needed. The following sub-sections detail the calculations performed to determine the energy absorbed per pulse as well as the resulting maximum average thermal temperature that could be reached in the irradiated volume. The decay of this temperature and the extent to which diffusion can facilitate the reaction of hot molecules at the cell walls are also investigated.

Estimate of Maximum Temperature

If all of the energy absorbed is distributed thermally among the degrees of freedom of SiF_4 and tetralin in a time short compared to energy loss processes, the maximum temperature, T_{max}, of the gas may be calculated.

The average energy absorbed per molecule is given by

$$E = \overline{E}_{abs} + E_o = 3kT_{max} + \sum_i \sum_j x_i g_{ij} \omega_{ij} \frac{e^{-hc\omega_{ij}/kT_{max}}}{(1-e^{-hc\omega_{ij}/kT_{max}})}$$

where $\overline{E}_{abs}$ is the laser energy absorbed divided by the number of molecules, SiF_4 plus 1, in the irradiated volume. E_o is the initial thermal energy of the system ($\overline{E}_{abs}$=0), g_{ij} is the degeneracy of vibrational mode ij having frequency ω_{ij}, and x_i is the mole fraction of molecule i. The maximum temperature, T_{max}, is solved for iteratively. The SiF_4 vibrational modes and degeneracies (in parentheses) used are, in cm^{-1} units, 260 (2), 420 (3), 800 (1), and 1040 (3). The 60 vibrational frequencies of tetralin were estimated roughly from the frequencies of benzene[11] and cyclohexene.[12] Accurate values for the tetralin vibrational frequencies are not required since 1 contributes only about 20% to the heat capacity even at the highest temperature. The estimated tetralin vibrational frequencies were grouped into six classes and average values used (See Table 1).

It should be noted that the cross-sectional area of the laser beam, and hence the irradiated volume, has a significant and systematic effect on the calculated T_{max}. Increase of the beam diameter from 0.70 to 0.75cm, for example, using the same total energy absorbed, would result in a T_{max} lower by about 200°. A rectangular or flat top beam profile is desired so that a constant temperature is reached across the entire irradiated volume. Use of an external iris with a large laser beam sharply defines the beam diameter but the intensity distribution across the beam is not well defined. An internal iris creates a more reproducible intensity distribution; however, there is a much less sharp cut-off at the fringe of the beam and a larger fraction of the energy in the lower energy wings of the

beam. Saturation in the SiF_4 attenuation cell can lead to a more strongly peaked spatial distribution which will vary with laser intensity. T_{max} can easily vary by 500°C between the center of the beam and a point at the beam's half-width. The calculated values of T_{max} do not give accurate temperatures; they do, however, provide a useful relative scale for comparing sensitized pyrolysis results.

Temperature vs. Time

Vibration-to-vibration (V→V) and vibration-to-translation and rotation (V→T,R) energy transfer insure that the absorbed energy is thermalized and the vibrations of 1 are excited within a few microseconds of the laser pulse. Within 100 collisions or about 2 μsec at 5 torr, thermalization by V→T,R should be nearly complete.[13] V→V transfer should pump the modes of 1 by nearly resonant transfer even more rapidly.

The laser-heated cylinder of gas is partially cooled by shock waves in a time given by the beam radius divided by the speed of sound at T_{max}. The temperature drop quenches reactions of sufficiently high activation energy. The amplitudes of shocks returning from the walls are too small to cause substantial further reaction. On a much longer timescale (several msec) heat conduction returns the sample to room temperature well before the following laser pulse. These points are illustrated by the infrared emission from the laser-heated gas (Figure 4). The emission between 1800-2400 cm^{-1} from the overtone of the laser-pumped SiF_4 mode is detected with a Cu:Ge detector with a 0.2 μsec response time. The peaks are the radial shockwaves and the overall decay (distorted by the low frequency amplifier cut-off) is the cooling by thermal conductivity.

Under the experimental conditions no significantly hot molecules

reach the cylindrical walls of the cell. Molecules at the wall are heated upon reflection of the shock wave but to a much lower temperature than T_{max}. A more significant problem in some systems may be surface reactions at the windows through which the laser beam must pass. However, less than 1% of the molecules in a 4 cm cell reach the windows while the temperature is near its maximum.

RESULTS

Multiphoton Dissociation

Tetralin has several absorption features of moderate intensity in the 10 m region of the infrared spectrum. This portion of the spectrum is shown in Figure 5 for a thin film of 1. The largest peak has an absorbance ten times smaller than the strongest absorbance features at 700 and 3000cm^{-1}. Figure 6 shows both thin film and gas phase spectra of the band irradiated during MPD experiments.

Irradiation of 0.325 Torr 1 with a focused CO_2 TEA laser at 946.0cm^{-1} produced products 2-7 (Figure 1) and an additional product, phenylacetylene. Styrene and phenylacetylene had similar GC retention times and could not be individually resolved. They were, however, differentiated by mass in the GC-MS analysis. No dissociation products were observed when the laser beam was unfocused.

The product distribution was studied as a function of the laser fluence to determine the effect of the up-pumping rate on the competing reaction channels. The results are listed in Table 2. The product yield of 2, the primary product of ethylene loss, and the combined yield of 6 + 7, the

products from the dehydrogenation channel, are shown in Figure 7. The retro-[2+4] cleavage is clearly the dominant reaction channel at low fluence. At a fluence of 23 J/cm^2, the ethylene-loss channel accounts for 73% of the total dissociation of 1 while only 6% of the dissociated 1 forms dehydrogenation products. At higher fluence, the percentage of the total reaction yield accounted for by 2 decreases and there is a marked increase in the yield of other products. These have been tentatively identified (by GC retention times and mass spectra) as toluene, ethylbenzene, 1,4-dihydronaphthalene, and o-ethylstyrene.

At all fluences employed except for the lowest (23 J/cm^2), a bluish- white emission was observed from the focal region. No attempt was made to either spatially or temporally resolve this emission. Visible emission from excited C_2 and CH is often observed in MPD of organic molecules under such focused conditions[14]. Fragmentation would complicate the observed product distribution. The observation of phenylacetylene, probably arising from dehydrogenation of excited styrene, is indicative of additional reactions not observed in flow pyrolysis or sensitized pyrolysis. GC-MS analysis of gaseous products showed that the acetylene/ethylene ratio increased from 0.59 to 1.15 as the fluence is increased from 35 to 75 J/cm^2, indicating high energy processes taking place at higher fluence.

Since MPD yield from 1 was relatively low and fragmentation apparently complicated the product distribution at high fluence, another technique was desired to investigate the unimolecular decomposition of 1.

SiF_4-sensitized Pyrolysis

SiF_4-sensitized pyrolysis of 1 results in products 2-7. A log-log plot of the total yield of dissociation products vs. energy absorbed per molecule (Figure 8) shows a linear relationship with a slope of 8. The absorbed energy, hence T_{max}, was varied by attenuating the incident laser energy with an SiF_4 attenuation cell or increasing the SiF_4 pressure in the pyrolysis cell. The pressure of 1 was 0.325 Torr and the SiF_4 pressure was between 5 and 10 Torr. The total dissociation yield of 1 was kept between 2 and 10% of the starting material in these experiments.

The product distribution in terms of the percentage of the total dissociation yield due to a single product is affected by the absorbed energy per molecule or T_{max} (Table 3). From the product distribution and sensitized pyrolysis of these materials (see later), 2, 4, and 6 apppear to be primary products while 3, 5, and 7 are predominantly secondary products. The yield of 2 and 4 increased relative to the other products as T_{max} decreased. The percentage yields of the primary products 2, 4, and 6, and the secondary products 3, 5, and 7, are shown in Figures 9 and 10 respectively. The absolute yield of the secondary products also increased more rapidly with increasing T_{max} than does the yield of primary products.

Another parameter which had an effect on the product distribution was the number of pulses used to irradiate the sample (N_p). The percentage of products 2, 4, and 6 decreased and the percentage of 3, 5, and 7 increased with increasing N_p. This is presumably due to dissociation of the accumulated primary products 2, 4, and 6 (see the following sub-section). Product 2 and ethylene are the primary products of the retro-(2+4) dissociation channel. Product 3 arises to some extent from secondary decomposition of 2. The ratio of products 3 to 2 as a function of N_p is

shown in Figure 11. The apparently non-zero intercept indicates that other channels of styrene production may exist which bypass 2.

Several experiments were performed to test for non-homogeneous processes during pyrolyses (Table 4). A pyrolysis was carried out in a 1.0cm long pyrolysis cell instead of the typical 3.85cm-long cell in order to investigate the possibility of surface catalyzed reactions. The increase in surface to volume did not alter the ratio of ethylene-loss to dehydrogenation. However, the four-fold decrease in volume decreased the total yield by a factor of 4.5. A pyrolysis was performed with the pressure of 1 reduced to 0.032 Torr. This appears to have no dramatic effect on the ratio of ethylene loss (2 + 3) to dehydrogenation (6 + 7). There is, however, an effect on the amount of secondary decomposition due to increased N_p. No products were observed when pyrolysis was performed without SiF_4. GC-MS analyses show no evidence of fluorine atom incorporation in the starting materials or products.

Decomposition of Primary Products

The primary products formed by the sensitized pyrolysis of 1 undergo subsequent dissociation under the pyrolysis conditions. Pure samples of 0.325 Torr of 2, 4, and 6 were each subjected to sensitized pyrolysis with 5 Torr of SiF_4. Less than 1/10 of this amount of 2, 4, and 6 were normally generated during a tetralin pyrolysis. The results of these pyrolyses are listed in Table 5. Sensitized pyrolysis of 2 resulted in isomerization to 3. Decomposition of 6 resulted in primarily 7 (68% of product) in addition to smaller quantities of 5, 1, 3, 1,4-dihydronaphthalene and six unidentified products. Sensitized pyrolysis of 4 produced a number of products, including 5 (24% of product), 1, 3, 6, and seven unidentified products. The

unidentified products observed in the dissociation of 4 and 6 are all observed to a very small extent in the sensitized pyrolysis of 1 carried out at high T_{max}. The efficiencies of decomposition of 2, 4, and 6 are all higher than the dissociation efficiency of 1.

Tetralin-d_4

Sensitized pyrolysis of 1-d_4 results in the distribution of isotopomers listed in Table 6. The results indicate that 2 arises solely from C_2H_4 loss from 1-d_4, exactly as one would expect from direct ethylene loss via retro-[2+4] cleavage. The dehydrogenation product is mostly 6-d_3 indicating that dehydrogenation occurs primarily as a result of 1,2-elimination.

The label distribution in products 3 and 5 is complex, indicating multiple channels for their formation. The effect of N_p on the observed distribution of isotopomers was studied to see what contribution of 3 arises from secondary decomposition of 2. The distribution of isotopomers is shown in Table 6. The percentage of 3-d_4 is substantially increased as the pyrolysis time increases indicating that 3-d_4 arises primarily from secondary decomposition of 2-d_4 at high N_p. The percentage of total product accounted for by the other isotopes of 3 remains relatively constant, 8.7 and 10.7% respectively for the 300 and 900 pulse pyrolyses.

Tetralin and tetralin-d_{12}

To examine the inter- or intramolecularity of the dehydrogenation, 1:2 mixture of 1-h_{12} and 1-d_{12} was pyrolyzed. The hydrogen from solely unimolecular dehydrogenation would be a mixture of H_2 and D_2. The results of mass spectral analysis of the hydrogen products are shown in Table 7. The

approximately 40% yield of HD indicates that hydrogen formation is significantly intermolecular. GC-MS analysis of the higher molecular weight products show substantial scrambling in 3 and 5. No scrambling was detectable in the starting 1-h_{12} or 1-d_{12} or in products 2, 4, 6, or 7. Subjection of a mixture of H_2 and D_2 to the pyrolysis conditions gave no detectable HD.

cis-Tetralin-d_{10}

The stereochemical relationship between two hydrogen atoms in cis-1-d_{10} allows the determination of the stereochemistry of the dehydrogenation reaction. A concerted cis-1,2-elimination of molecular hydrogen or deuterium would result exclusively in 6-d_8 and 6-d_{10}. The isotopic distribution of products 6 and 7 are shown in Table 8. The large amount of 6-d_9 observed indicates that a step-wise loss of hydrogen is taking place. A large percentage of 7-d_7 (48%) is also observed.

DISCUSSION

Energetics of the Ethylene-loss Channel

A concerted mechanism for the retro-[2+4] reaction of 1 would involve o-xylylene (10) as an intermediate (see Figure 12). Loss of benzene resonance in the formation of 10 would be expected to cause an increase in the activation energy of the retro-[2+4] reaction relative to that of the analogous process in cyclohexene.[15] An estimate of this increase may be obtained by comparing reactions which generate 10 with analogous olefinic reactions. Two model reactions which may reflect this destabilization of the transition state for the reaction are the ring opening of benzocyclobutene

and the loss of HCl from α-chloro-o-xylene.[16] Comparison of these reactions with the ring opening of cyclobutene and the loss of HCl from 1-chloro-2-methyl-2-butene respectively, shows that the increase in activation energy for those reactions involving 10 is approximately 8 kcal/mole. If this difference is added to the E_a for the cyclohexene retro-[2+4],[15b] an activation energy of 75 kcal/mole is obtained for a concerted retro-[2+4] reaction of 1.

The $\Delta H_f^o(298)$ of 9, the diradical intermediate in a stepwise process can be estimated using group additivity parameters.[17] This is calculated to be 67 kcal/mole above the $\Delta H_f^o(298)$ of 1. We therefore consider it very likely that the retro-[2+4] reaction of 1 proceeds by a stepwise process, involving intermediate 9.[18] The observation of 4, the disproportionation product of 9, is good evidence for the presence of 9. Definitive tests of the stepwise or concerted nature of the retro-[2+4] reaction of 1 await suitable stereochemical labelling studies.[21]

Mechanism of Dehydrogenation

The mechanism for this reaction channel contrasts with that of cyclohexene.[22] The labelling data from 1-d_4 indicate that 80-85% of the dehydrogenation results in loss of hydrogen from C-1 and C-2 of 1. The data from 1-d_{10} and the mixed isotope experiments indicate that a large fraction of the dehydrogenation channel is intermolecular, i.e. non-concerted. A simple model for the dehydrogenation channel involving a combination of a concerted 1,2-elimination and a non-concerted 1,2-hydrogen elimination can be applied to this system.

The dehydrogenation channel can be modeled most closely by a 1,2-

elimination, since the 1-d_4 labeling data indicate the majority of the reaction is occuring by this pathway. An isotope effect can be estimated to be between 1.5 and 2.0 at the reaction temperatures based on the difference in the zero-point energies of C-H and C-D bonds. Assuming an isotope effect[23] of 2.0 on the overall formation of H_2 and D_2 in the crossover experiment, then a 1:2:1 mixture of H_2:HD:D_2 would be expected for a completely random stepwise mechanism. Since the observed result is 3:4:3, some contribution to the experimental ratio may be due to a concerted, molecular hydrogen loss. Assuming an isotope effect of 2.0 for a concerted hydrogen elimination, under the experimental conditions, a ratio of 1:1 of H_2:D_2 would result for a completely concerted elimination. A combination of 20% concerted elimination and 80% stepwise loss would give rise to the observed ratio of 3:4:3 for H_2:HD:D_2.

Applying these same assumptions to a completely stepwise reaction of cis-1-d_{10} results in a calculated ratio for H_2:HD:D_2 of 1:3:2.25. A completely concerted 1,2-elimination (with an isotope effect of two and appropriate statistical corrections) would give rise to an H_2:D_2 ratio of 1:1.5. A 20% contribution of a concerted path and an 80% contribution of the stepwise path would give rise to an H_2:HD:D_2 ratio of 2:4:4, which is approximately the ratio inferred from Table 8. Thus, an approximately 20% contribution of a concerted, molecular hydrogen elimination is consistent with both sets of experiments using this simple model. This data, however, by no means proves the existence of a concerted pathway in the dehydrogenation.

Two reasonable candidates for the stepwise mechanism are depicted in Figure 13. Thermochemical calculations were carried out for both pathways using group additivities.[17] The thermodynamic quantities for each elementary

step at 1302°K were estimated using the following equations:

$$\Delta H^{o}_{1302} = \Delta H^{o}_{f298} + \Delta C^{o}_{p800}(T-T_o)$$

$$\Delta S^{o}_{1302} = \Delta S^{o}_{298} + \Delta C^{o}_{p800}\ln(T/T_o)$$

where ΔH^{o}_{f298}, S^{o}_{298}, and C^{o}_{p800} for each molecule were calculated from group equivalent tables. Values for ΔG^{o}_{1302} were then calculated to get an estimate for the relative rates for each step. The ΔG^{o}_{1302} for the rate determining steps 1 and 3 were estimated to be 47±5 and 48±5 kcal/mole respectively, unfortunately too close to allow a distinction to be made between the two pathways. Franz[6g] has shown that two key intermediates in this reaction scheme, the 1-tetralyl and 2-tetralyl radicals (13 and 12 respectively, generated from the corresponding t-butyl peresters at 900°K), form 1,2-dihydronaphthalene.

Mechanism of Formation of Styrene and Indene

The time dependence of the isotopic distribution of styrene shows that when the number of pulses is large, the majority of styrene is derived from benzocyclobutene. At low conversion there appear to be multiple channels for styrene formation, as shown by the labeling results from 1-d_{10} and 1-d_4. The mixed isotope experiments indicate that there are also intermolecular mechanisms for styrene's formation. The details of the mechanisms for these reaction channels are not known.

The time and temperature dependence data both support the formation of indene as a secondary product. The labelling data from 1-d_4 is consistent with indene arising primarily from o-allyltoluene and 1,2-dihydronaphthalene.

CONCLUSION

The thermolysis of tetralin appears to give rise to three primary dissociation channels: one involving ethylene loss resulting in benzocyclobutene, the second involving ring cleavage resulting in o-allyltoluene, and the third involving hydrogen loss giving rise to 1,2-dihydronaphthalene. Interestingly, the ring cleavage product o-allyltoluene has not previously been reported as a product in the thermal reactions of 1. We believe this is due to the efficiency with which it decomposes under the reaction conditions. This points to an important advantage of utilizing lasers in the study of gas phase thermal reactions: the exposure time of molecules to the high temperature reaction conditions is extremely short, resulting in relatively little secondary decomposition of primary products.

We have also discovered that the lowest energy reaction channel for the dissociation of 1 is the ethylene-loss channel. In all previous investigations the predominant reaction was dehydrogenation. We believe that this was due to catalysis of this reaction channel by hot surfaces.[1e] This points to another striking advantage of laser-assisted dissociation studies: the experiment can be designed so that surface catalysis of reactions at the cell walls or windows is insignificant, thus resulting in truly homogeneous thermal reactions.

The details of the overall mechanism for the dissociation of tetralin to the three primary products can be thought of most simply in two ways: one involving the diradical intermediate 9 as a precursor to all primary products (see Figure 14) or a partitioning of the three channels at 1 (instead of at 9). The formation of 9 as an intermediate in the ethylene-

loss channel appears to be energetically favored over the concerted reaction. Although the labeling data are consistent with 80% of the dehydrogenation channel being a stepwise hydrogen loss, neither these data nor thermochemical calculations implicate (or rule out) 9 as an intermediate in the dehydrogenation channel.

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18. There are numerous examples that show that the rates of disproportionation and recombination reactions of 1,6-diyls are within a factor of three, usually favoring disproportionation.[19] From Benson's estimate[17] for ring closure of 6-vinyl-hex-2-ene-1,6-diyl diradical (log A = 12, E_a = 1 kcal/mole), the rate constant for disproportionation can be estimated to be 6.0 x 10^{11}/sec at 1000°K. Since the ratio of 3/2 is approximately 0.3 at 1000°K, the rate constant for ethylene loss must be approximately 1.8 x 10^{12}/sec. Using the frequency factor derived for ethylene loss from hex-2-ene-1,6-diyl ($10^{13.5}$/sec),[20] an E_a for ethylene loss from 9 is calculated to be 6 kcal/mole.

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23. We have attempted to measure the isotope effect on the rate of appearance of 6 and 6-d_{10} by utilizing a beam splitter and two photolysis cells, one containing 1 and the other containing 1-d_{12}. We are not confident that the reaction conditions were identical in each cell and thus that the number obtained (1.2-1.4) was accurate. However, we do expect that the isotope effect will be small at these temperatures.

Figure 1. The major products from the thermal dissociation of tetralin are shown. They are benzocyclobutene (2), styrene (3), o-allyltoluene (4), indene (5), 1,2-dihydronaphthalene (6), and naphthalene (7).

Figure 2. A schematic diagram of the apparatus used for SiF_4-sensitized pyrolysis experiments. The iris (0.7 cm diameter) is designated by I, A is the attenuation cell, BS is the NaCl beam splitter and PM 1 and PM 2 are power meters.

Figure 3. The synthetic sequences for deuterium-labeled tetralin.

Figure 4. The infrared fluorescence at 5 μm from an SiF_4-sensitized pyrolysis cell containing 5 Torr of SiF_4. The upper curve (a), shows the fluorescence observed when the laser beam passed directly through the center of the pyrolysis cell. The lower curve (b), shows the fluorescence observed when the laser beam passed through the cell off-center, displaced from the cell axis toward the detector. The beam axis was 1.5 cm from the center of the cell and 0.7 cm from the cell wall. The laser energy was 0.20 J/pulse in a 0.7 cm diameter beam. The droop of the baseline below zero is due to the amplifier response.

Figure 5. The infrared spectrum of a thin film of 1 between NaCl plates in the 900-1100 cm^{-1} range. The resolution is 1 cm^{-1}. The arrow at 1027.4 cm^{-1} is the frequency of the laser line used for the SiF_4 photolyses. The arrow at 946.0 cm^{-1} is the frequency of the laser line used for MPD.

Figure 6. The infrared spectrum of 1 in the 915-975 cm^{-1} range. The solid curve is the spectrum of gas phase 1 (0.4 Torr) taken with a path length of 9.75 m and a resolution of 1 cm^{-1}. The dashed curve is a thin film spectrum of 1. The absorbance scale refers only to the gas phase spectrum. The arrow at 946.0 cm^{-1} is the frequency of the laser line used for MPD.

Figure 7. The yield of 2 and the yield of the dehydrogenation products 6 and 7 as a function of fluence in the MPD of 1 at 946.0 cm^{-1}.

Figure 8. A log-log plot of the total decomposition of 1 (sum of the product yields of all high (>90) molecular weight products vs energy absorbed per molecule in SiF_4-sensitized pyrolyses of 1. The slope is 8.5. A 0.7 cm diameter laser beam (external iris) at 1027.4 cm^{-1} was used with a 3.85 cm long pyrolysis cell. The pressure of 1 was 0.325 Torr and the SiF_4 pressures were 5, 5, 6, and 8 Torr, from left to right.

Figure 9. The yield of the primary products of the decomposition of 1 in terms of the percentage of total products vs T_{max} in the SiF_4-sensitized pyrolysis of 1.

Figure 10. The yield of the secondary products of the decomposition of 1 in terms of the percentage of total products vs T_{max} in the SiF_4-sensitized pyrolysis of 1.

Figure 11. The ratio styrene to benzocyclobutene (3/2) produced in the SiF_4-sensitized pyrolysis of 1 vs the number of laser pulses used in the experiment. The experiments were performed with 0.325 Torr 1, 5.0 Torr SiF_4, a 0.7 cm diameter beam, external iris, 3.85 cm path length and a laser energy of 0.27 J/pulse. The calculated T_{max} was 1400°C.

Figure 12. Two possible mechanisms for the production of 2 from 1. The concerted pathway proceeds via intermediate 10 and the non-concerted pathway involves stepwise C-C bond cleavage proceeding initially via intermediate 9. The non-concerted pathway presumably also leads to the production of o-allyltoluene.

Figure 13. Two possible mechanisms for the production of 1,2-dihydronaphthalene (6) from 1. The upper pathway proceeds via initial C-H bond cleavage and the lower pathway proceeds via initial C-C bond cleavage. Both pathways produce free H atoms.

Figure 14. A mechanism for the production of all primary products from the dissociation of 1 involving the common intermediate 9.

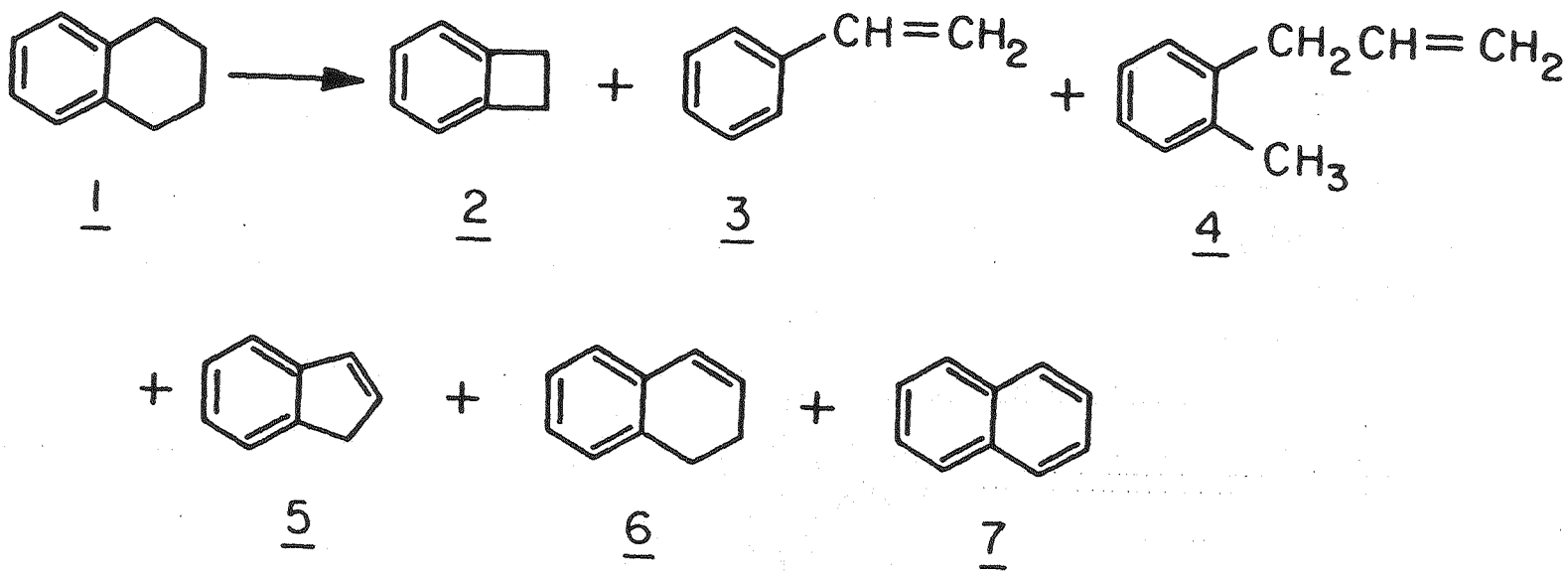

Fig. 1

XBL 811-5038

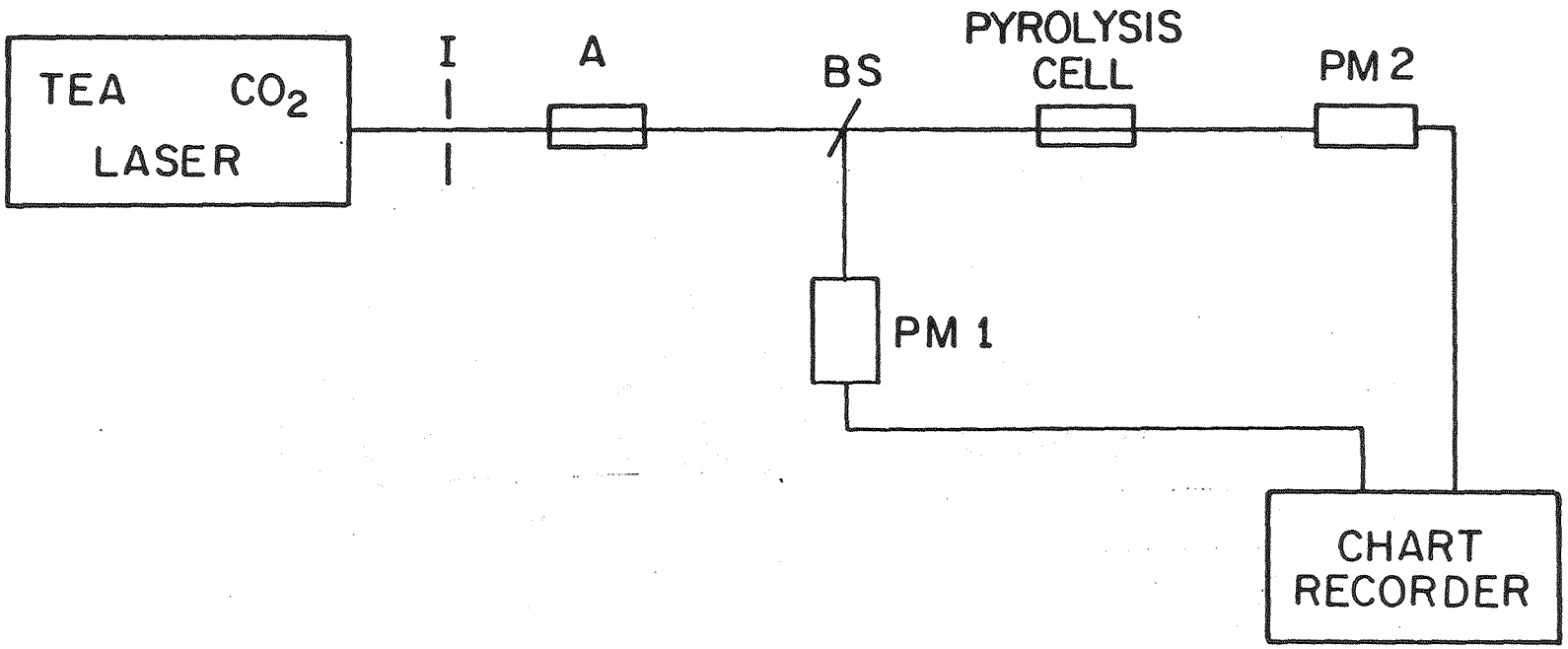

Fig. 2

XBL 811-5062

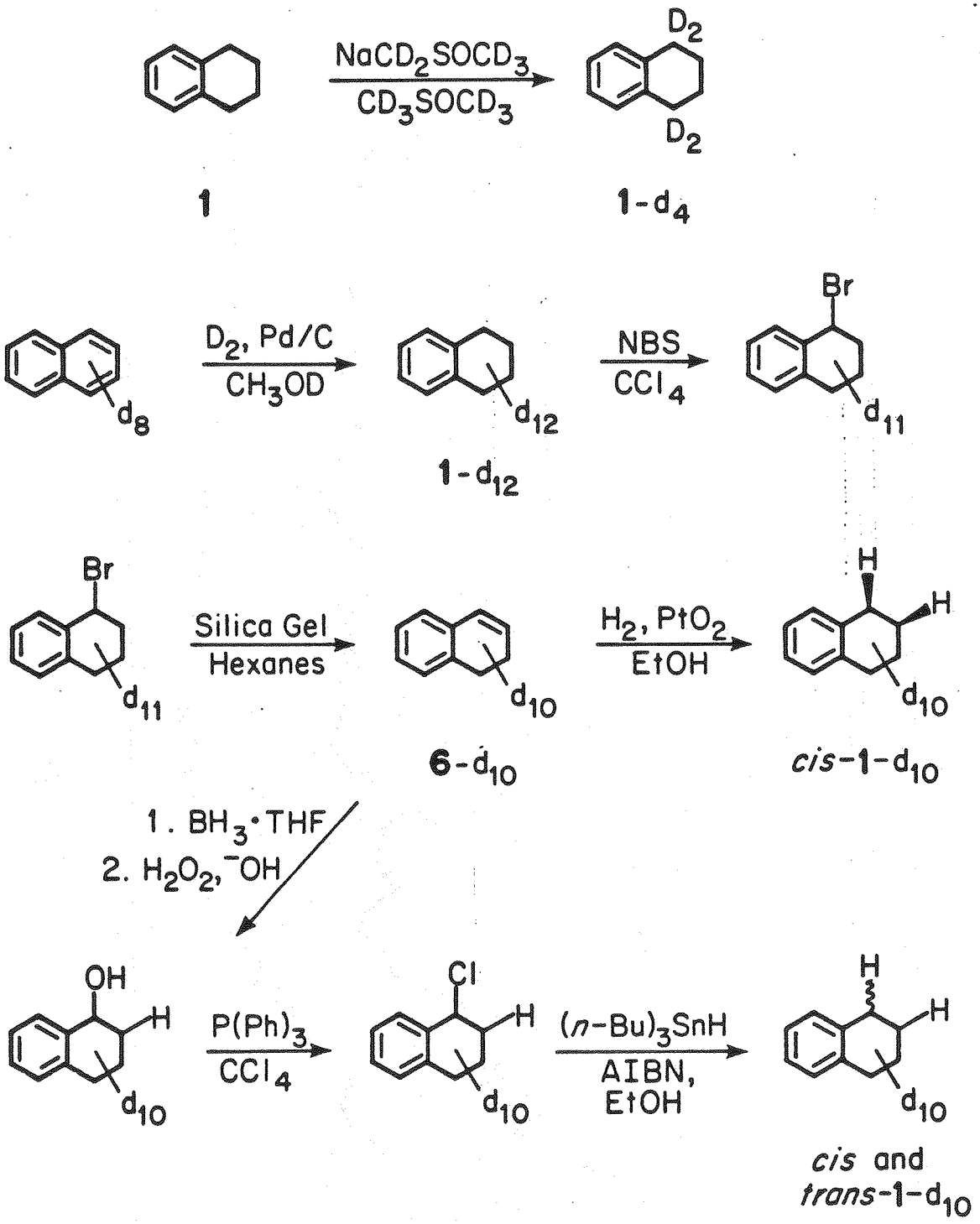

Fig. 3

XBL 814-9160

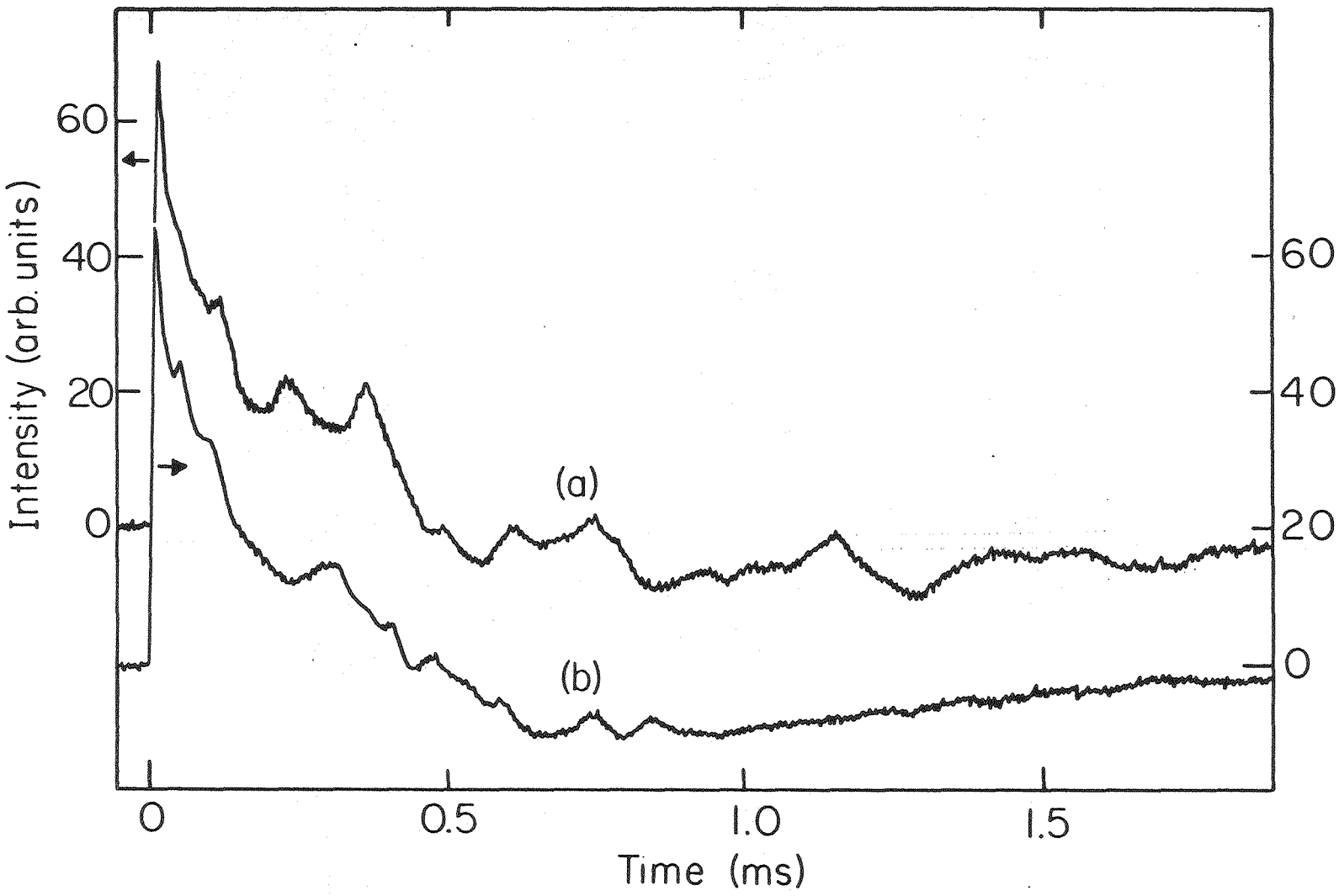

Fig. 4

XBL 811-5063

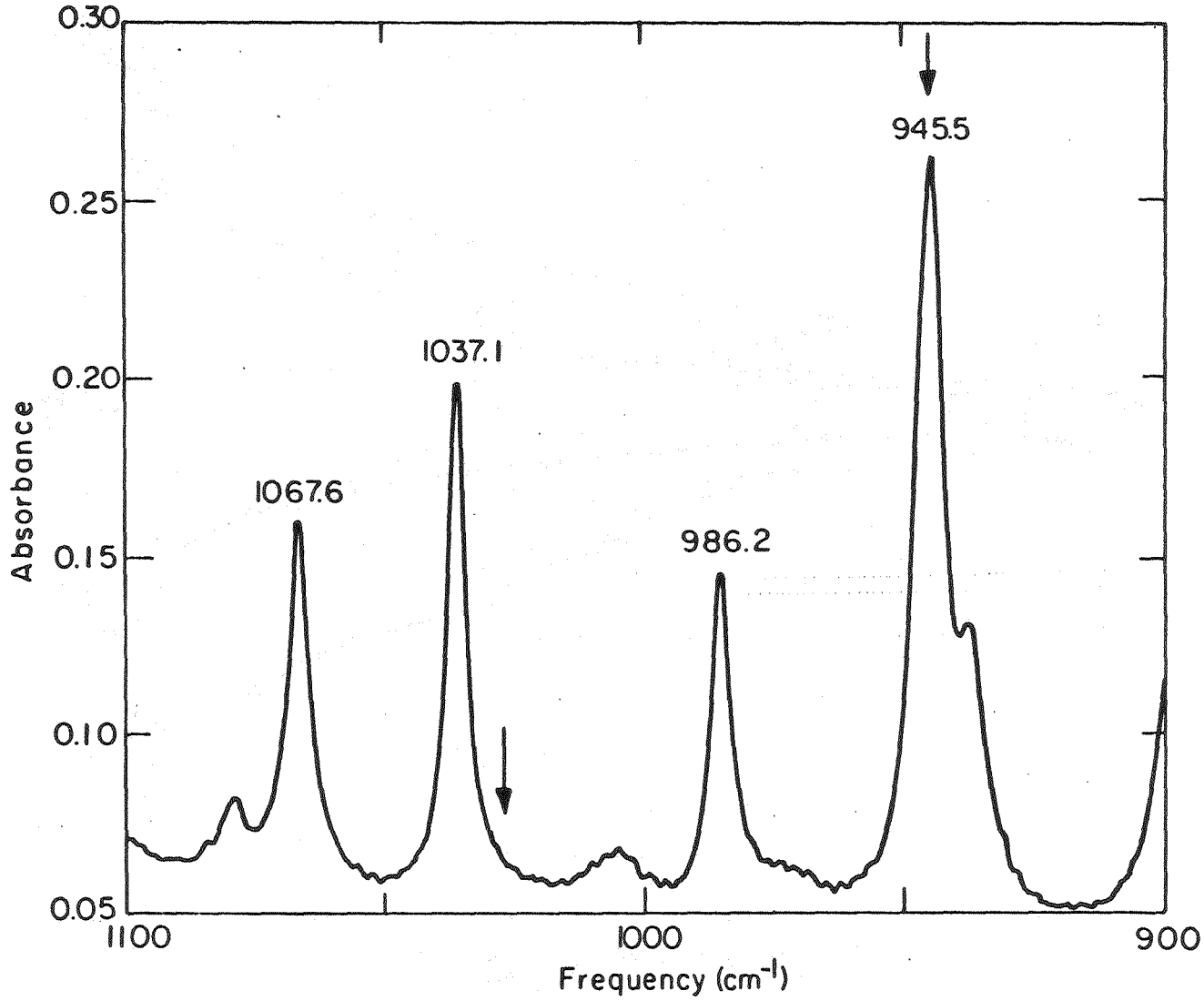

Fig. 5

XBL 811-5047A

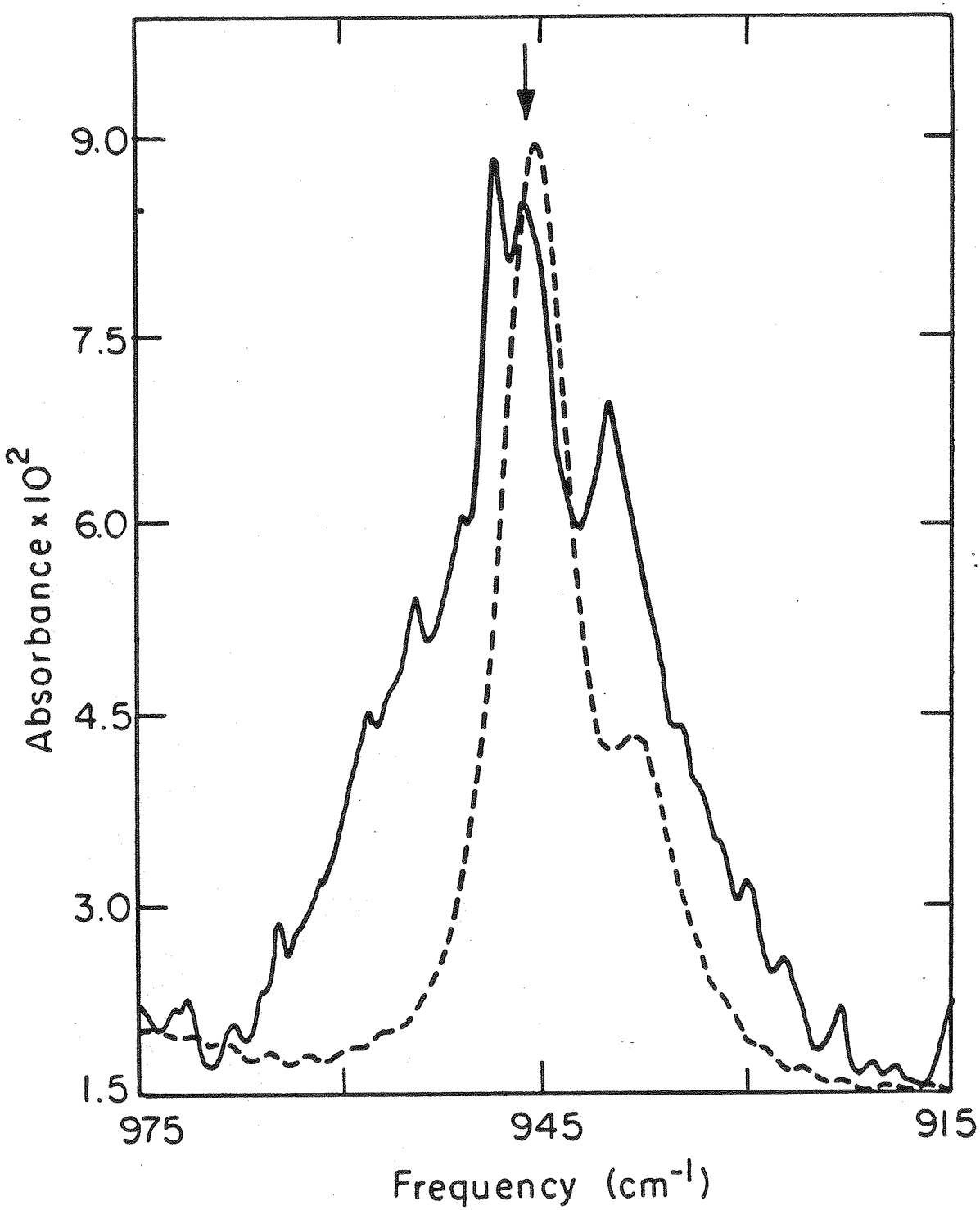

Fig. 6

XBL 811-5046A

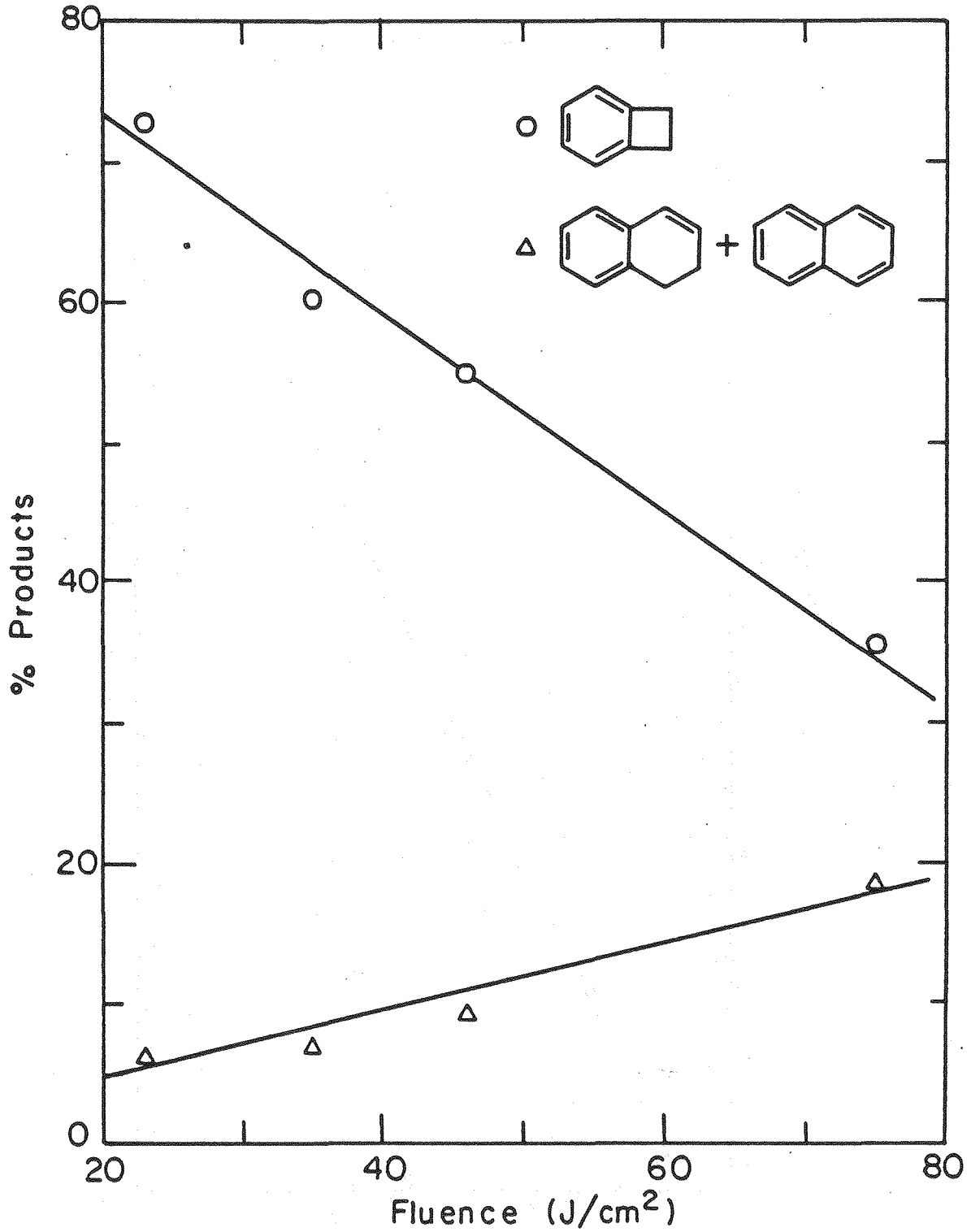

Fig. 7

XBL 811-5057

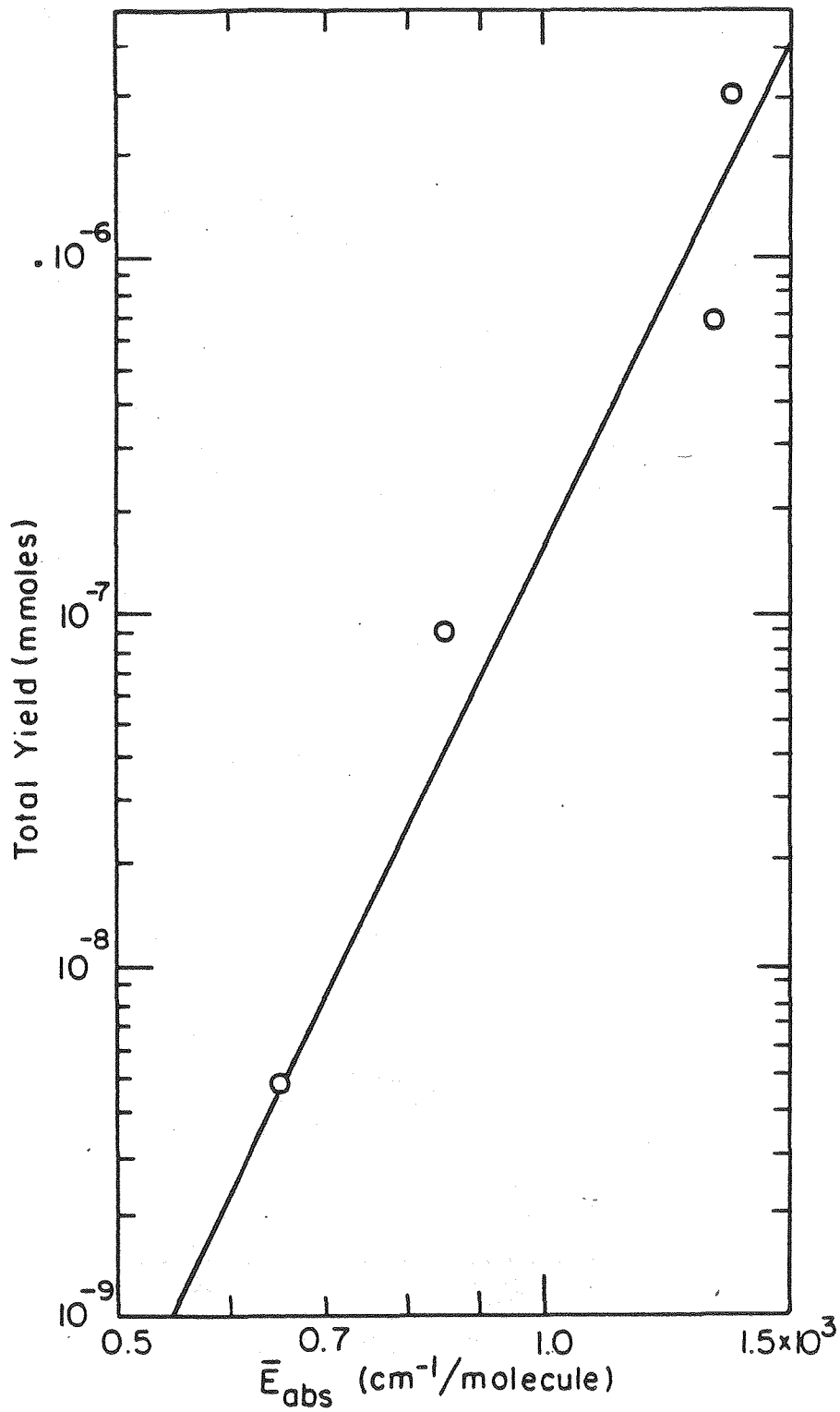

Fig. 8

XBL 811-5037

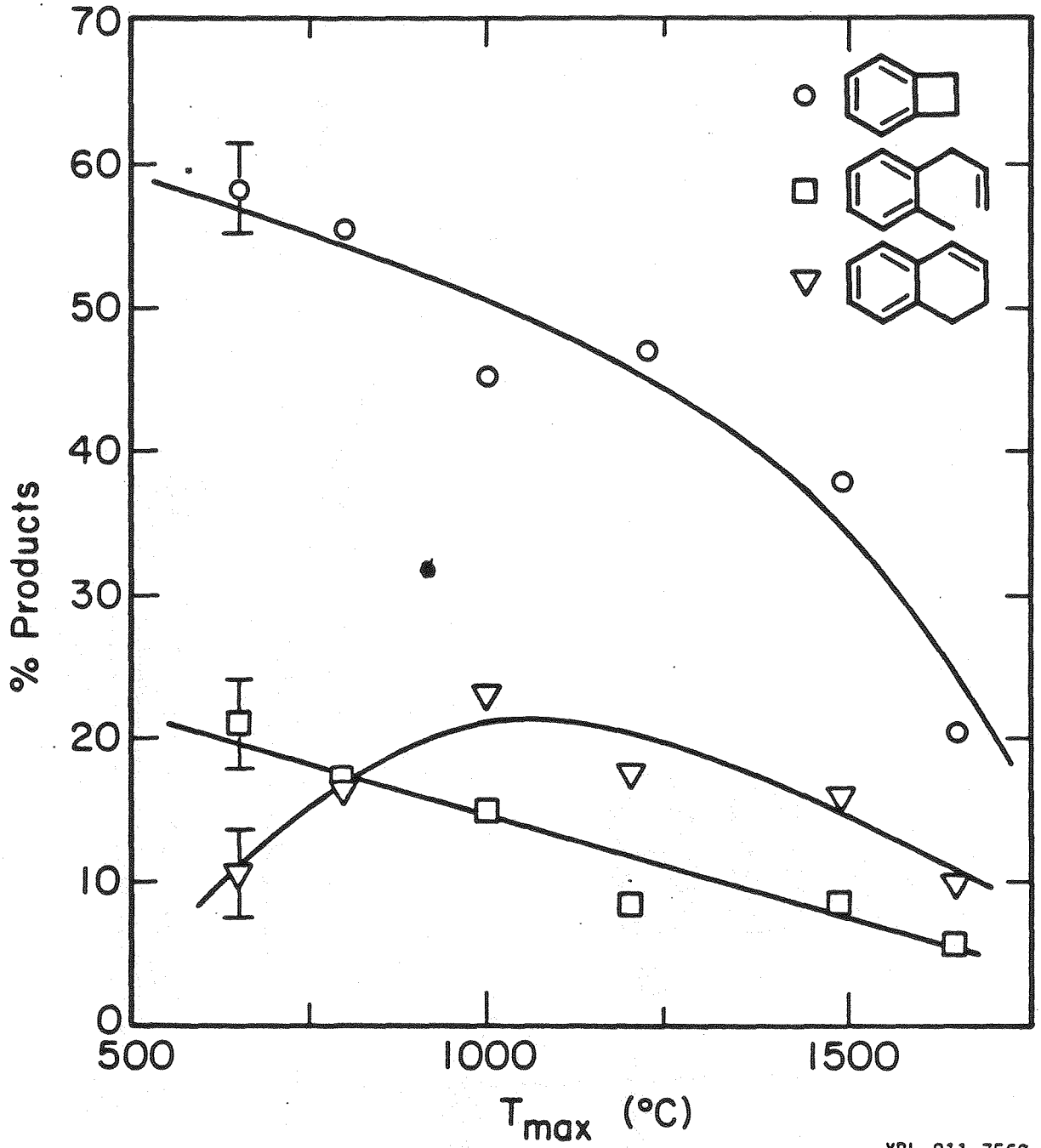

Fig. 9

XBL 811-7569

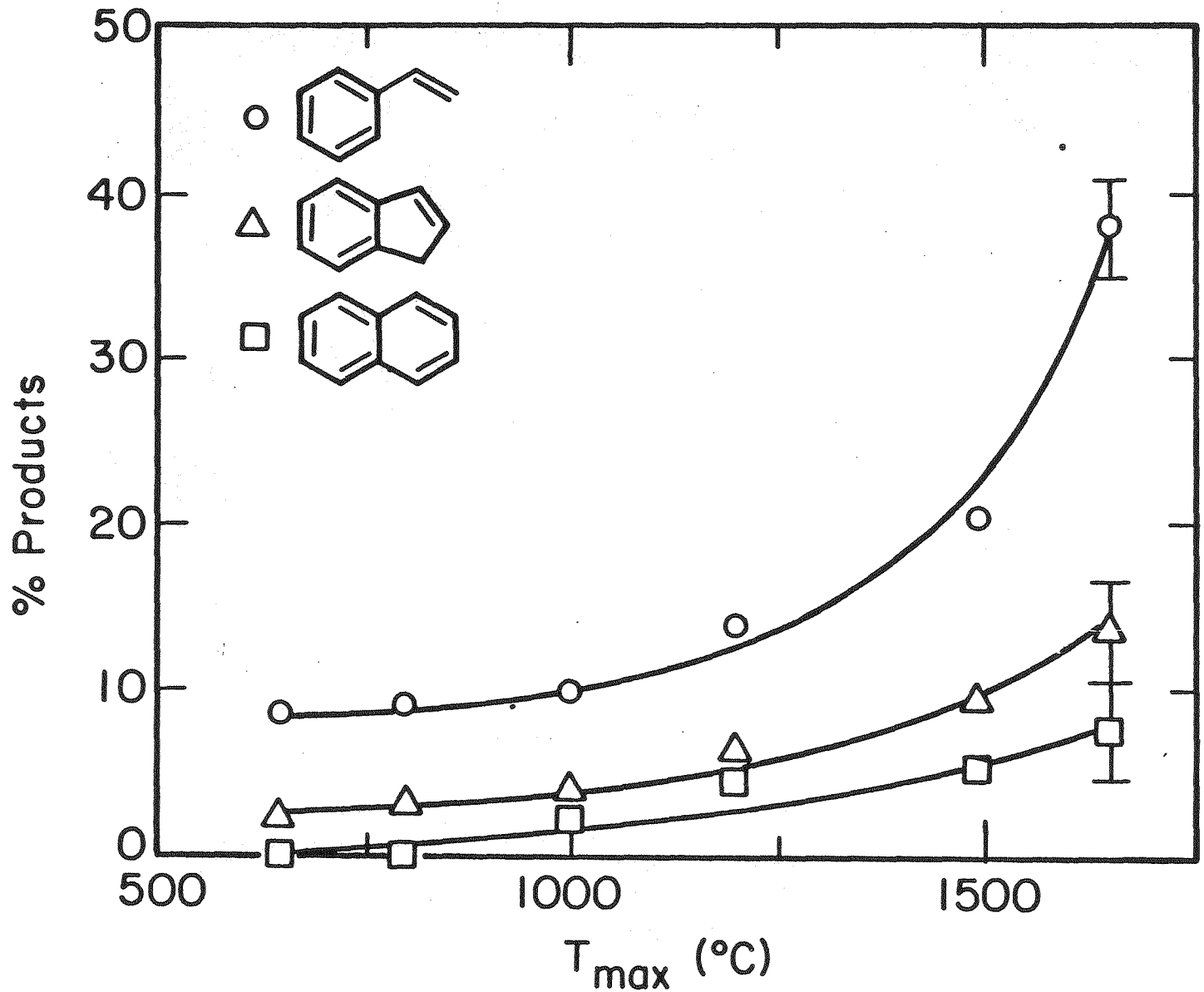

Fig. 10

XBL 811-7568

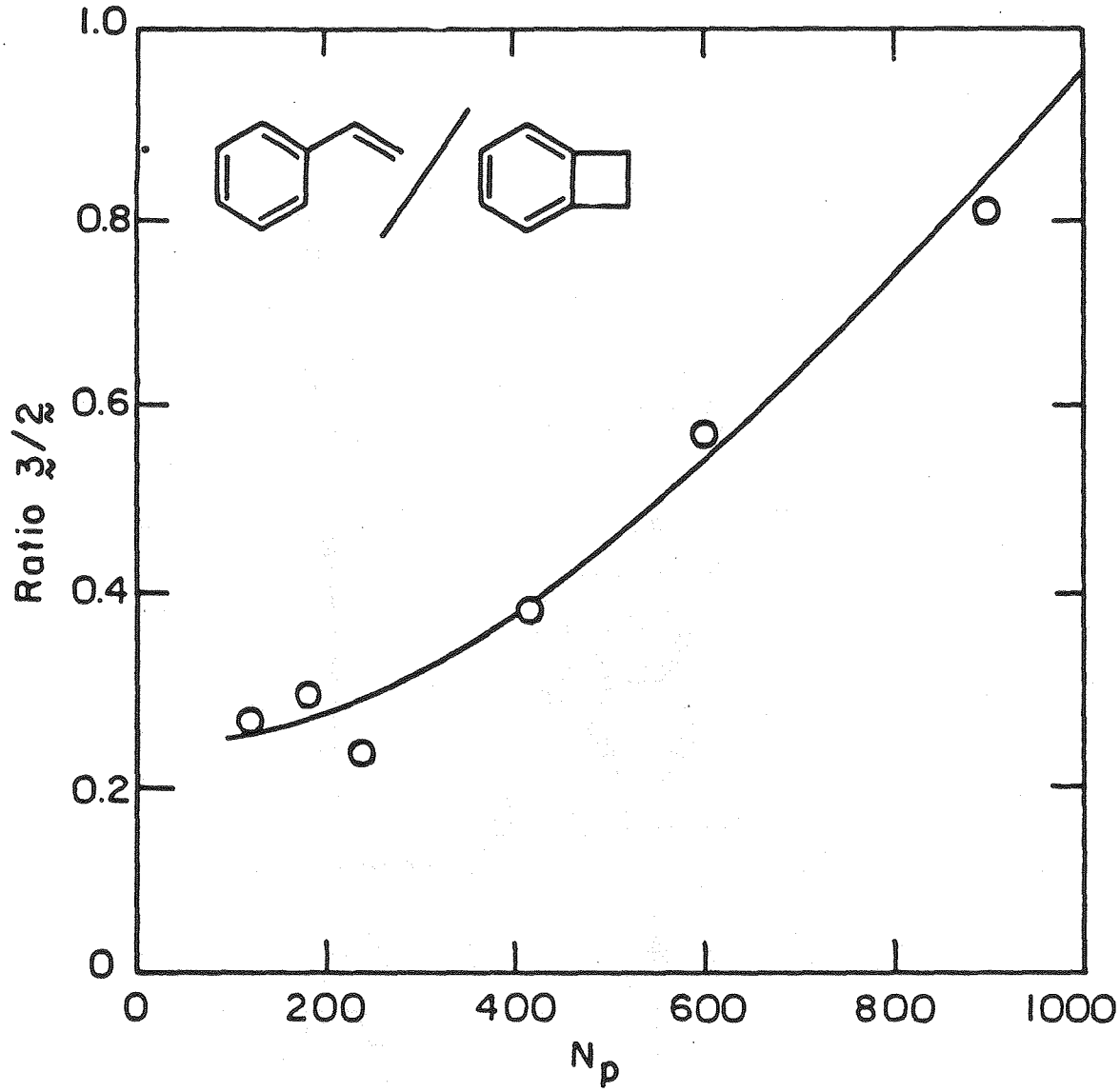

Fig. 11

XBL 811-5058A

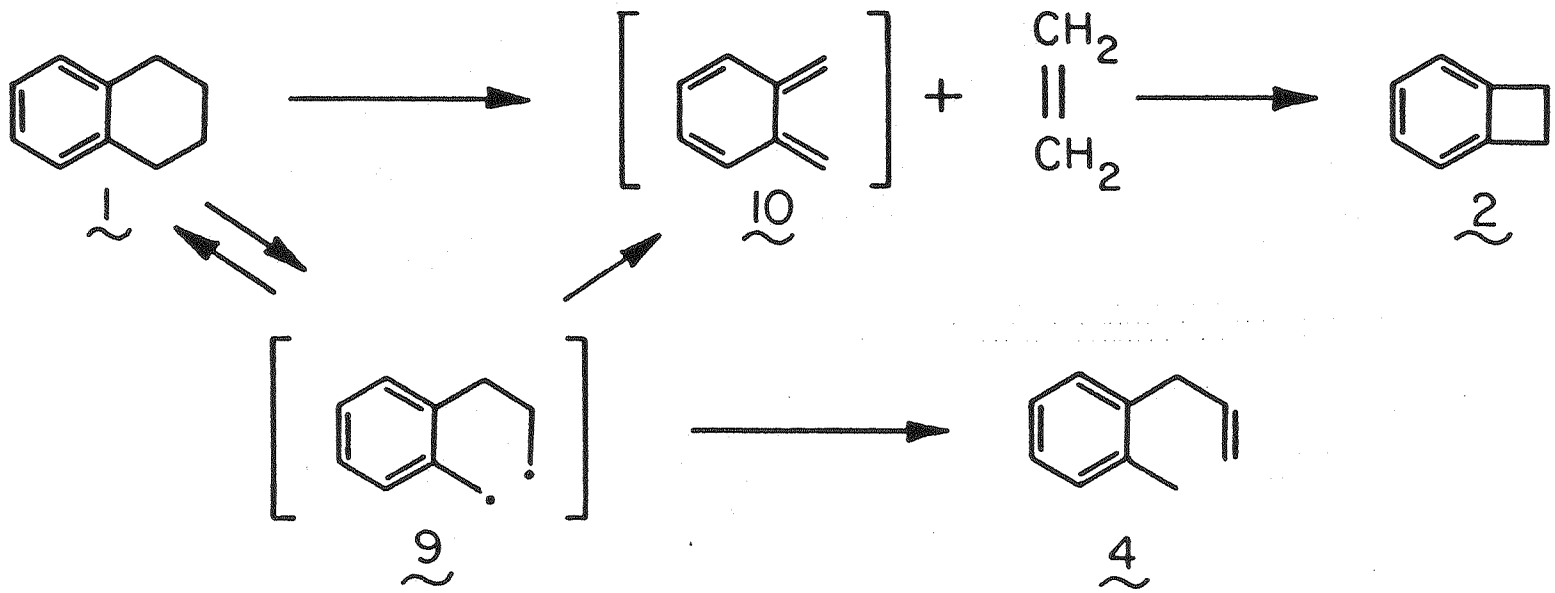

Fig. 12

XBL 811-5042

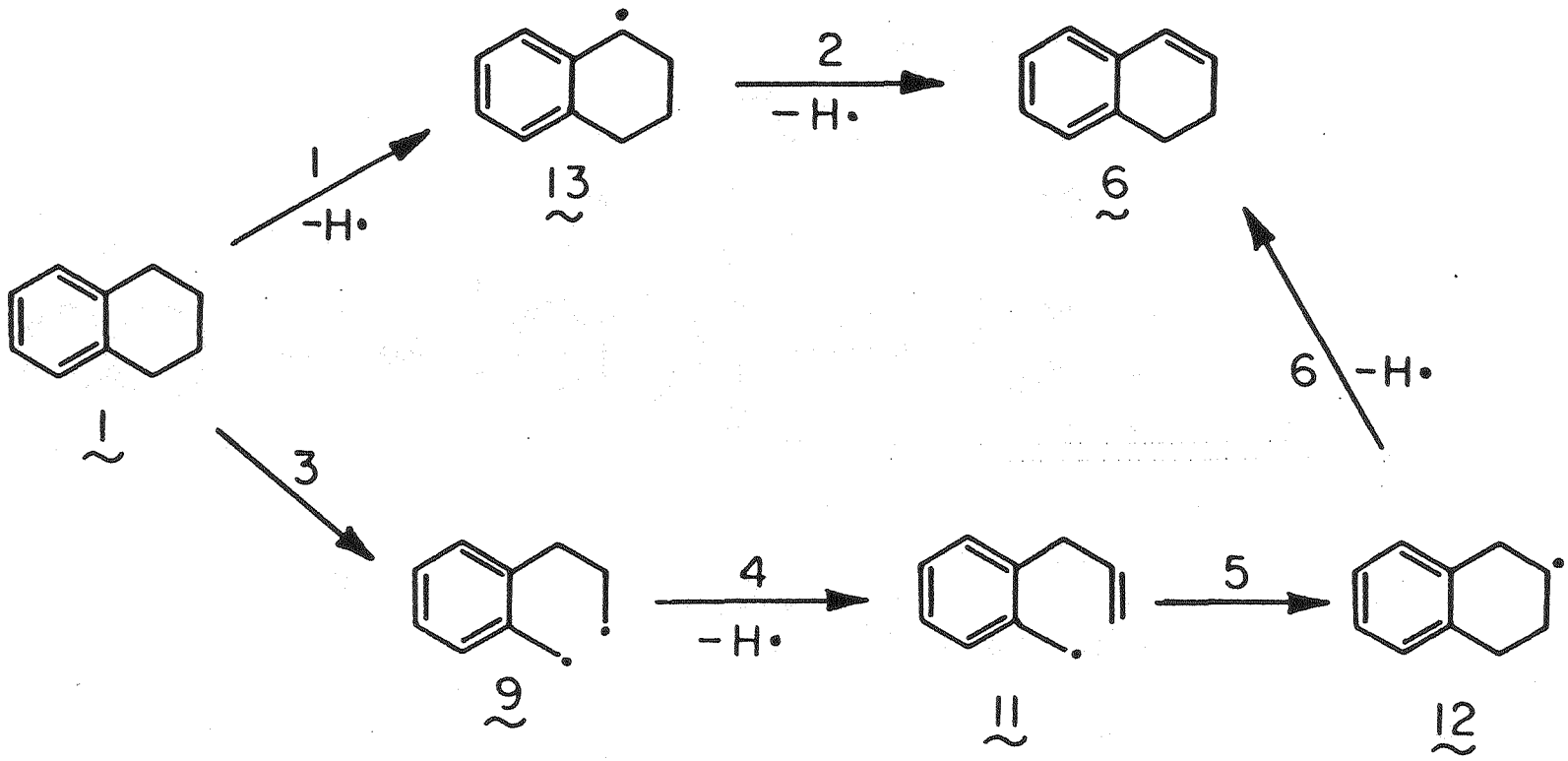

Fig. 13

XBL 811-5039

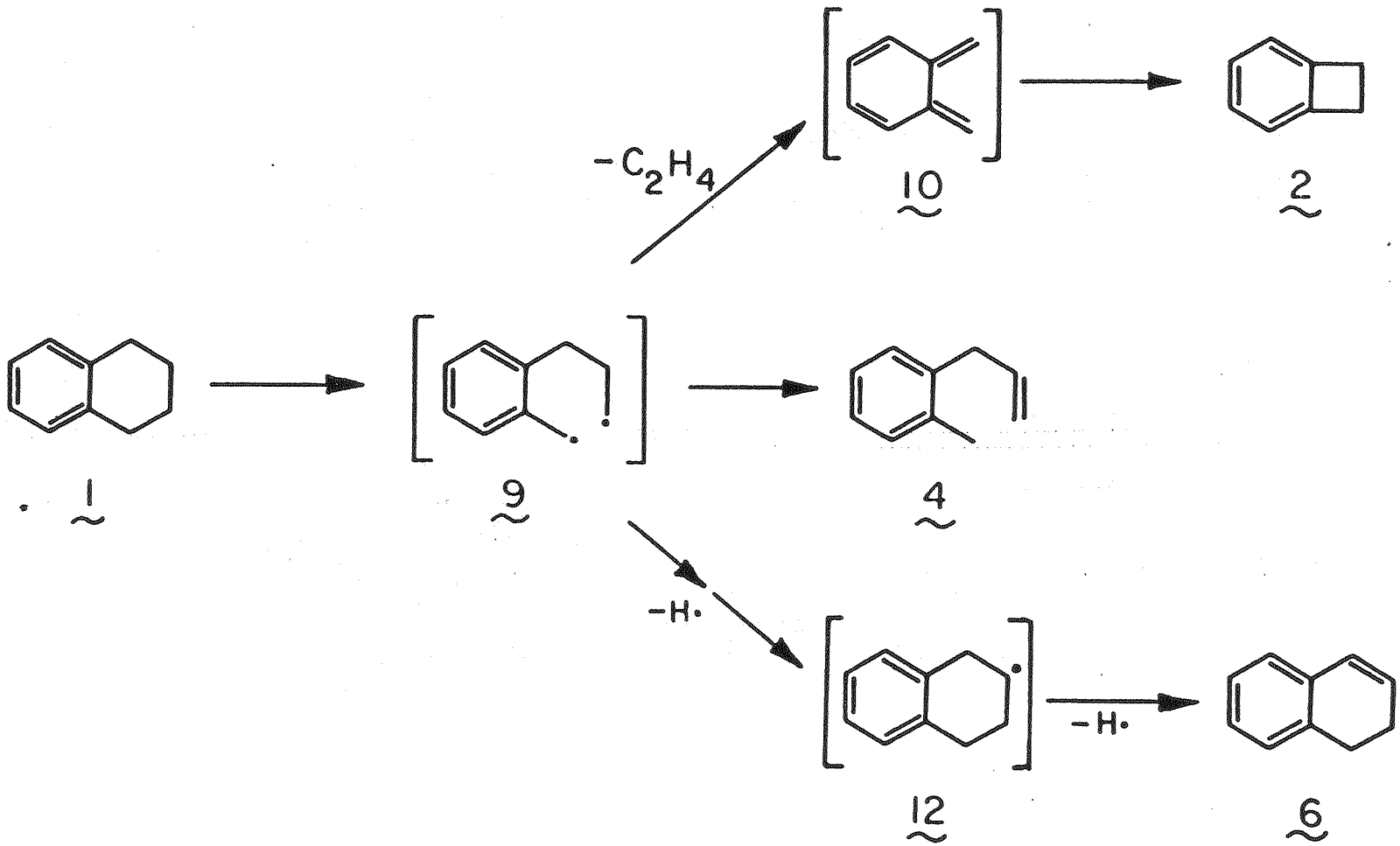

Fig. 14

XBL 811-5040

Table 1. Vibrational frequencies of benzene, cyclohexene and tetralin (in cm^{-1} units)

Benzene	Cyclohexene	Tetralin[a]
398 (2)[b]	236 (2)	236 (2)
608 (2)		
674	507 (4)	541 (10)
707		
846 (2)	791 (4)	833 (8)
967 (2)	905 (2)	
990	970 (2)	
995	1060 (3)	1051 (13)
1010	1127 (2)	
1037 (2)		
1146		
1178 (2)	1247 (4)	
1309	1363 (2)	1412 (15)
1350	1438 (6)	
1482 (2)	1667 (1)	
1585		
1606		
3038		
3047		
3056 (2)	2922 (10)	2960 (12)
3057		
3073		

[a]Vibrational frequencies for tetralin are estimates.

[b]Numbers in parentheses are degeneracies.

Table 2. Product distribution from MPD of tetralin

Fluence (J/cm^2)	Pulses ($x10^3$)	Products (%)							% Conversion of 1
		2	3[a]	4	5	6	7	Other	
23	12.6	72.6	11.7	3.4	4.2	6.2	0.0	2.0	0.4
35	3.6	60.0	22.9	2.3	5.2	6.8	trace	2.9	0.4
46	2.7	54.8	19.7	2.6	5.5	9.0	trace	8.4	0.8
75	2.7	35.5	9.9	7.2	10.6	9.9	8.8	18.1	1.7

[a]Includes response of phenylacetylene.

Table 3. Product distribution from SiF_4-sensitized pyrolysis of tetralin[a]

P_{SiF_4} (Torr)	E_{inc} (J)	T_{max} (°C)	Pulses ($x10^2$)	Products (%)						Other	% Conversion of 1
				2	3	4	5	6	7		
5.0	0.11	650	49.6	58.5	8.3	20.8	2.2	10.3	0	0	1.5
5.0	0.14	800	37.2	55.5	9.0	16.8	2.7	16.0	0	0	0.7
5.0	0.18	1000	16.7	45.2	10.0	14.8	3.9	22.7	2.2	1.3	2.8
5.0	0.21	1220	1.8	47.3	12.9	8.0	6.4	17.3	4.9	3.3	4.7
6.0	0.27	1490	1.8	38.2	20.1	8.4	9.4	15.5	5.6	2.8	7.7
10.0	0.21	1650	0.15	20.4	38.2	5.6	13.7	9.9	7.6	4.6	1.7

[a]Tetralin pressure = 0.325 Torr, external iris, 0.7 cm beam, 3.85 cm cell length.

Table 4. Tests for non-homogeneous reactions in SiF_4-sensitized pyrolysis of 1

Conditions[a]	E_{inc} (J)	Np	Products (%)							% Conversion of 1
			2	3	4	5	6	7	Other	
cell length = 1.0 cm	0.27	1200	24.0	35.0	8.4	8.3	14.2	8.5	1.5	28.0
0.080 Torr 1	0.25	1200	22.6	30.8	6.5	8.9	13.3	12.4	5.5	31.4
0.030 Torr 1	0.26	3000	7.6	56.0	1.8	7.6	5.3	20.1	1.6	54.6

[a]Pyrolysis conditions: SiF_4 pressure = 5.0 Torr, tetralin pressure = 0.325 Torr, 3.85 cm cell length, 0.7 cm beam, except where noted.

Table 5. Sensitized pyrolysis of 2, 4, and 6

Parent	E_{inc} (J/pulse)	T_{max}[a] (°C)	Pulses	Products (%)									% Conversion
				1	2	3	4	5	6	7	8[b]	Other	
2	0.21	1200	300	-	x	100.0	-	-	-	-	-	-	69.8
4	0.18	1000	100	4.7	-	1.8	x	24.3	1.7	-	-	67.7[c]	16.0
6	0.21	1200	300	5.2	-	2.7	-	10.5	x	68.1	7.5	5.9[d]	21.7

[a] T_{max} calculated using the heat capacity of tetralin instead of that for 2, 4, or 6.

[b] 8 is 1,4-dihydronaphthalene.

[c] 7 products.

[d] 6 products.

Table 6. Deuterium labeling in products from sensitized pyrolysis[a] of $\underset{\sim}{1}$-d_4

Product	Pulses	% of Total Products	Isotopomer (%)			
			d_4	d_3	d_2	d_1
$\underset{\sim}{2}$	300	47.3	100.0[b,c]	0	0	0
	900	31.9	100.0	0	0	0
$\underset{\sim}{3}$	300	12.9	32.4	8.1	28.7	30.8
	900	25.5	58.1	10.7	16.0	15.2
$\underset{\sim}{4}$	300	8.0	100.0	0	0	0
	900	7.9	100.0	0	0	0
$\underset{\sim}{5}$	300	6.4	0.5	42.0	42.5	15.1
	900	7.1	4.5	41.4	40.4	13.6
$\underset{\sim}{6}$	300	17.3	9.6	83.0	7.3	0
	900	15.9	8.6	80.9	10.5	0
$\underset{\sim}{7}$	300	4.9	0	1.2	94.6	4.1
	900	4.7	0	20.1	72.3	7.6

[a]Pyrolysis conditions: $\underset{\sim}{1}$-d_4 (0.325 Torr) was irradiated with 300 or 900 pulses, 0.27 J/pulse, with 5 Torr SiF_4. T_{max} was 1430°C.

[b]The numbers are the percent of product with the indicated number of deuterium atoms as determined by GC-MS analysis.

[c]The data are corrected for ^{13}C natural abundance and 98.7% deuterium incorporation in $\underset{\sim}{1}$-d_4.

Table 7. Hydrogen product from the sensitized pyrolysis of mixtures of $\underset{\sim}{1}$-h_{12} and $\underset{\sim}{1}$-d_{12}[a]

Run	Sample $\underset{\sim}{1}$-h_{12} (Torr)	Sample $\underset{\sim}{1}$-d_{12} (Torr)	Products, % H_2	HD	D_2
1.	0.15	0.34	30.0	39.8	30.3
2.	0.16	0.34	29.7	38.8	31.5
3.[b]	0.16	0.34	27.1	42.0	30.9

[a] SiF_4 pressure = 5 Torr, laser intensity = 0.20 J/pulse, T_{max} = 1120°C.

[b] Same pyrolysis as 2 but this spectrum taken 5 min after run 2 with the sample constantly flowing into the mass spectrometer.

Table 8. Deuterium labeling in dehydrogenation products from sensitized pyrolysis[a] of $\underset{\sim}{1}$-d_{10}

Product	Isotopomer, %				
	d_{10}	d_9	d_8	d_7	d_6
$\underset{\sim}{6}$	21.5[b]	38.5	40.1	0	-
$\underset{\sim}{7}$	-	-	37.9	49.1	13.0

[a]Pyrolysis conditions: 1-d_{10} (0.325 Torr) was irradiated with 1000 pulses, 0.19 J/pulse, with 5 Torr SiF_4. T_{max} was 1050°C.

[b]The data are corrected for ^{13}C natural abundance and 97.8% deuterium incorporation in $\underset{\sim}{1}$-d_{10}.