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STUDIES ON PHOTOCHEMICAL REACTIONS
OF SIMPLE ALKENES

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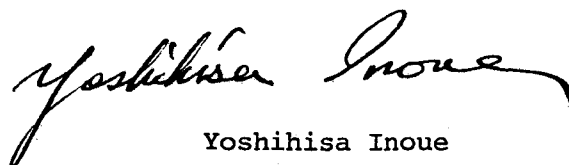JANUARY, 1977

Preface

The work of this thesis was performed under the guidance of Professor Hiroshi Sakurai at the Institute of Scientific and Industrial Research, Osaka University.

I am deeply grateful to Professor Hiroshi Sakurai for his appropriate guidance and continuous encouragement throughout this work since 1972. I am also grateful to Professor Yoshinobu Odaira who initiated me into the organic photochemistry in 1971-1972.

I am indebted to Assistant Professor Setsuo Takamuku for his invaluable discussions throughout the work. Many thanks are given to Drs. Yoshiki Okamoto, Chyongjin Pac, Susumu Toki, and Yasuo Shigemitsu for their helpful suggestions through the stimulating discussions with me. I would like to express my gratitude to Mr. Kazuyoshi Moritsugu, Mr. Masahiro Kadohira, and Ms. Yoko Kunitomi for their collaborations in the course of experiment. Finally I wish to thank all the members of Sakurai Laboratory for their warm friendship.

Yoshihisa Inoue

Suita, Osaka
January, 1977

List of Papers

The contents of this thesis are composed of the following papers.

1) Mercury Photosensitized Reaction of Cycloheptene. Mechanism of Norcarane Formation
   Y. Inoue, M. Kadohira, S. Takamuku, and H. Sakurai,
   Tetrahedron Lett., 459(1974).

2) Vapor-phase Photolysis of cis- and trans-4,5-Dimethylcyclohexenes
   Y. Inoue, S. Takamuku, and H. Sakurai,
   Bull. Chem. Soc. Jpn., 48, 3101(1975).

3) Photochemical Rearrangement of Cycloheptene
   Y. Inoue, S. Takamuku, and H. Sakurai,
   J. Chem. Soc. Chem. Comm., 577(1975).

4) Intramolecular Hydrogen Abstraction of the Vibrationally Excited Triplet State of Simple Alkenes
   Y. Inoue, S. Takamuku, and H. Sakurai,
   J. Chem. Soc. Chem. Comm., 896(1975).

5) Sensitized Photolysis of cis-Cyclooctene Vapour
   Y. Inoue, K. Moritsugu, S. Takamuku, and H. Sakurai,
   J. Chem. Soc. Perkin II, 569(1976).

6) Vapor-phase Photolysis of cis-Cyclononene
   Y. Inoue, S. Takamuku, and H. Sakurai,
   Bull. Chem. Soc. Jpn., 49, 1147(1976).

7) An Anomalously High trans:cis Photostationary Ratio on the Direct Photo-isomerization of Cyclooctene
   Y. Inoue, S. Takamuku, and H. Sakurai,
   J. Chem. Soc. Chem. Comm., 423(1976).

8) Mercury Photosensitization of 1-Hexene and cis-2-Octene Vapor. Intramolecular Hydrogen Abstraction of Vibrationally Excited π,π^* Triplet State
   Y. Inoue, S. Takamuku, and H. Sakurai,
   Can. J. Chem., 54, 3117(1976).

9) Direct and Sensitized cis-trans Photoisomerization of Cyclooctene. Effects of Spin Multiplicity and Vibrational Activation of Excited States on Photo-stationary trans/cis Ratio
   Y. Inoue, S. Takamuku, and H. Sakurai,
   J. Phys. Chem., in press(January, 1977).

10) Direct Photolysis of Cycloalkenes
    Y. Inoue, S. Takamuku, and H. Sakurai,
    J. Chem. Soc. Perkin II, in press.

11) Direct cis-trans Photoisomerization of Cyclooctene. A Convenient Method for Preparing trans-Cyclooctene
    Y. Inoue, S. Takamuku, and H. Sakurai,
    Synthesis, in press.

Contents

Introduction

Progress has been rapid in organic photochemistry during the last two decades. The selective introduction of energy into individual molecule by means of absorption of light provides a unique approach to effecting chemical transformations in organic molecules, and a wide variety of new photo-induced reactions, which are of importance in both synthetic and mechanistic aspects, has come to our knowledge. The rapid accumulation of the knowledge in organic photochemistry makes possible the systematic interpretation of the photochemical reactions particularly of aromatic and carbonyl compounds. Recent interest in photochemistry may be found in the further understanding of the correlation between the electronic states involved and their chemical reactivities. Although, with the complicated electron-systems containing various excited states, such discussions have actually made, the detailed investigations with more simplified electronic systems are desired in order to further clarify the electronic state-reactivity relationship.

Ethylene and its alkyl-derivatives, which are at the foundation of our understanding of unsaturated compounds, provide a suitable system for investigating the photochemical behaviors of pure, simplest 2π-electron system. Considering the fundamental position of these simple alkenes, it is surprising that little effort has been directed toward the systematic understanding of their photochemical reactivities, although the photo-physics of these molecules have rather been known (see below).

Energetics and Dynamics

1 Emission rare (S_1, T_1);

$$\phi_F, \phi_P < 0.01$$

2 Large S_1-T_1 separation;

$$\phi_{S \to T} < 0.01$$

3 Rapid torsional motion for S_1, T_1

4 Rapid internal conversion $(S_1 \to S_o^*)$

5 Rydberg excited state (Ry);

little information

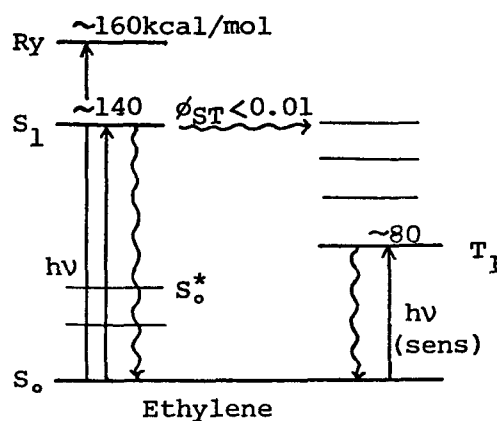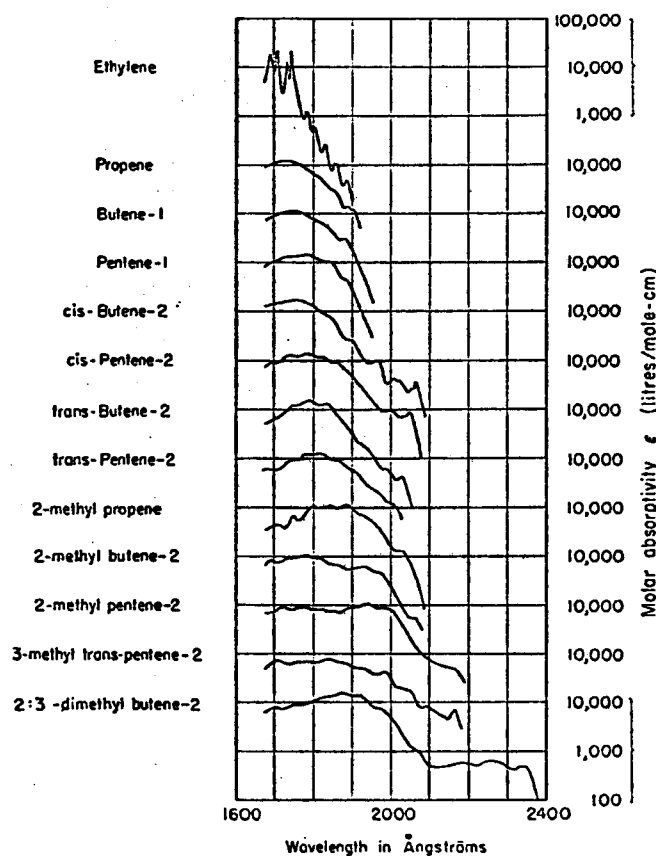Fig. 1. Photophysics of Simple Alkenes

Fig. 2. Far-ultraviolet spectra of some simple
alkenes; L. C. Jones, Jr. and L. W.
Taylor, Anal. Chem., 27, 278(1955).

This is partly due to the absence of the effective absorption band in an accessible uv region above 230 nm, as shown in Fig. 2. In view of the present situation of the alkene photochemistry, it is not only valuable to investigate and systematize the photochemistry of simple alkenes, but such studies will also provide beneficial informations for discussing the photochemical reactions of other unsaturated compounds. One of the main intentions of this thesis is to reveal the chemical reactivities of the electronically excited states generated in the direct and sensitized photolyses of simple alkenes. Furthermore, the auther wishes to discuss the effects of spin states and vibrational activation of the excited states on their rectivities.

Chapter 1 deals with the direct photolysis at 185 nm of cycloalkenes (C_6-C_9) in the vapor and liquid phases. The chemical behaviors of π,π^* excited singlet and $\pi,R(3s)$ Rydberg state will be clarified. A synthetic application of the direct photolysis is also described. Chapter 2 deals with the photosensitized reaction of simple alkenes (C_6-C_9) in the vapor

phase.   Novel reactions via vibrationally-excited triplet state and their detailed mechanism will be described.   In connection with the elecronic state-reactivity relationship, Chapter 3 deals with the comparative studies of direct and sensitized photolyses.   In the first section of the chapter, the emphasis will be placed on the spin correlation effects on the stereochemistry of the reaction and also on a "hot, triplet" biradical intermediate generated on vapor-phase photosensitization.   The second section deals with the photochemical cis-trans isomerization of cyclooctene.   The drastic effects of spin multiplicity and vibrational activation on the photostationary state of cyclooctene will be discussed.

Chapter 1   Direct Photolysis of Cycloalkenes

While a variety of studies has been made on the photochemistry of alkyl-substituted ethylenes, the great majority of these works concerned with the triplet sensitization and therefore with the chemical reactivities of the alkene triplet thus generated.   On the other hand, photochemical behaviors following direct excitation of these compounds are known less, partly because of the absence of the effective absorption in the uv region above 230 nm.   Limited studies on the vapor-phase photolysis[1] have shown that, when directly irradiated, an alkene is promoted to an excited singlet state and then suffers fast internal conversion to afford a vibrationally excited ground-state molecule; this species is known to undergo the allylic C-C and/or C-H bond cleavages in addition to the cis-trans isomerization by collisional deactivations.   On liquid-phase direct photolysis, apart from the cis-trans isomerization and the allylic fissions, the stereospecific cyclodimerization of 2-butene[2] and the photorearrangements via carbene intermediates of tetrasubstituted alkenes[3] have been recently reported. However, little comparative study on the vapor- and liquid-phase photolysis has been made, although such a study makes possible a comprehensive understanding of the fates of the excited states involved and their subsequent chemical reactions.

Further interest may be found in the possible photochemical formation of the highly strained trans-cyclohexene and trans-cycloheptene upon direct irradiation of their cis-isomers.   In the field of the cycloalkene chemistry, many efforts have been made for generating the strained trans-cyclo-alkenes.[4]   These trans-cycloalkenes were postulated in some cases as an unstable intermediate which give rise to an addition product with (acidic) methanol[5] or isobenzofuran derivative.[4]   However, it always remains uncertain whether free trans-cycloalkenes are formed under these reaction conditions and, if exist, how long is the lifetime of these strained compounds, since all the reactions employed were carried out in the presence of the trapping agents.

In this chapter, the electronically excited states generated on the direct photolysis at 185 nm of cycloalkenes (C_6-C_9) and their chemical reactivities will be discussed.   The auther also presents a definitive evidence in support of the formation of highly strained trans-cyclohexene and trans-cycloheptene in their ground electronic states upon direct irradiation of these cis-isomers.

Experimental .

<u>Materials.</u>———— Commercially available cyclohexene(<u>1a</u>), cycloheptene(<u>1b</u>), and cis-cyclooctene(cis-<u>1c</u>) were used after the purification by fractional distillation through a spinning-band column and/or preparative gas chromatography to purities of >99.9, >99.9, and 99.5%, respectively. The experimental sample of cis-cyclooctene contained a small amount(0.46%) of cyclooctane but was free from the trans-isomer.

trans-Cyclooctene(trans-<u>1c</u>) was prepared by a three-step process starting from its cis-isomer, according to the method reported previously.[6] Fractional distillation under a reduced pressure of the product gave the experimental sample of trans-<u>1c</u>, which contained 0.38% of the cis-isomer as an impurity. A correction was made for the impurity in the determination of the product yields.

cis-Cyclononene(cis-<u>1d</u>) was prepared from cyclononanol. Cyclononanol, prepared from dimethyl azerate according to procedures similar to those described in "Organic Syntheses,"[7] was heated with phosphoric acid to yield cis-cyclononene, which was purified to 99.5% by preparative glc.

Cycloheptene-1,2-d$_2$(<u>1b</u>-d$_2$) was prepared in a four-step synthesis. Cycloheptanone was converted to cyclohepta-1,2-dione by oxidation with selenium dioxide.[8] Then the deuterated cycloheptene <u>1b</u>-d$_2$ was synthesized by LiAlD$_4$ reduction of the cycloheptadione to cycloheptan-1,2-diol-1,2-d$_2$, followed by bromination of the diol with phosphorous pentabromide[9] to 1,2-dibromocycloheptane-1,2-d$_2$ and subsequent debromination with zinc powder[10] to give the product <u>1b</u>-d$_2$(99.9% pure), the isotopic purity of which was confirmed to be 98.0% by nmr and mass spectrometry.

The solvent n-pentane was shaken with concentrated sulfuric acid, washed with water, dried over potassium carbonate, and fractionally distilled prior to use.

<u>Analysis.</u>———— Gas chromatographic analysis of the reaction products from the direct photolyses of <u>1a</u>, <u>1b</u> or <u>1d</u>, and <u>1c</u> were carried out using a 9 m column of 20% β,β'-oxydipropionitrile(ODPN) at 30°C, a 6 m column of 15% polyethylene glycol-6000(PEG) at 70°C, and a 6 m column of 20% ODPN at 70°C, respectively. The analyses of the methoxycycloalkenes(<u>6</u>) were performed on a 3 m column of 15% PEG at 100-150°C. All products, which can be separated from each other under these conditions, had retention times on glc and mass spectra identical with those of commercially obtained or independently synthesized authentic specimens. As an internal standard, cyclo-

heptane, cyclooctane, and n-octane were employed for the liquid-phase photo-
lyses of 1a, 1b, and 1c, respectively.

Vapor-phase photolysis.——— All experiments in the vapor phase were carried
out at room temperature and under static conditions. Cylindrical cells,
5 cm long and 5 cm in diameter, made of Suprasil and a mercury-free vacuum
system were employed for the vapor-phase photolysis. The irradiation at
185 nm was run using a spiral array of 30 W low-pressure mercury lamp with
a Suprasil envelope, the light path being flushed with nitrogen gas during
the irradiation. The lamp was allowed to warm up for at least 30 min be-
fore each run in order to reach a stable operating condition. Control
runs revealed that no detectable reaction occurred under irradiation through
a Toshiba UV-25 filter which removes the 185 nm-resonance line of mercury,
suggesting the incompetence of the another intense 254 nm-resonance line for
the direct photolysis.

 After each run, products were trapped in a capillary at -196°C; small
amounts of the non-condensable products were discarded. The condensables
were subjected to the analysis on glc.

Liquid-phase photolysis.———Pentane solution containing 0.01 M cycloalkene
(1a-c) and a trace amount of the internal standard was irradiated at 185 nm
(as the effective resonance line of mercury) by a 30 W U-shaped low-pressure
mercury lamp fitted with a immersion reactor under nitrogen atomosphere.
The product yields following direct irradiaiton was determined by glc analy-
sis of aliquots removed from the irradiated solution. The liquid-phase
photolyses of the deuterium labelled cycloheptene 1b-d$_2$ and non-deuterated
cycloheptane 1b were run at a concentration of 0.066 M in a Suprasil cell,
1 cm X 1 cm X 5 cm, under external irradiation by the low-pressure mercury
lamp.

 Liquid-phase photolyses of 0.01 M cyclohexene and cycloheptene in the
presence of 0.50 M methanol and/or 0.03 M concentrated sulfuric acid were
carried out in the immersion reactor under similar conditions. Control
runs revealed that the substrate cycloalkenes 1, and the products 4 and 5
as well, did not react with acidic methanol to give the methoxycycloalkanes
6 even after standing the acidic cycloalkene solution for one day without
uv irradiation.

Photolysis at lower temperature.——— When the whole equipment employed
for the liquid-phase photolysis at room temperature was immersed into a
dry ice-acetone bath, satisfactory radiation from the lamp could not be

obtained because of the extremely low vapor pressure of mercury at the temperature. Liquid-phase photolyses at -78°C were therefore carried out by external irradiation method in the cylindrical Suprasil vessel used for the vapor-phase experiments. A pentane solution(5 ml) containing 0.01 M cycloheptene was placed in the cylindrical cell, and then deaerated by five freeze-thaw cycles in a mercury-free vacuum system. The bottom half of the cell, where the solution lay, was cooled to -78°C and the solution was irradiated externally through the top window of the cylinder by the spiral mercury lamp. After the irradiation, the irradiated solution was divided into desired number of portions with continued cooling at -78°C. In the determination of the lifetime of trans-cycloheptene, the divided porsions were kept at -10±2°C for definite periods, and then chilled in turn to -78 °C. Subsequently, a large excess of pre-cooled methanol(at -78°C) containing 5% concentrated sulfuric acid was added onto the treated solution, and the mixture was gradually warmed up to room temperature with vigorous shaking.

Photochemical one-step synthesis of trans-cyclooctene.——— Since the syntheses of trans-cyclooctene so far reported require a number of steps and/ or the use of relatively inaccessible starting materials[11] which may offset their good yields(~75%), a more convenient method has been desired. The photochemical cis→trans isomerization is considered to provide a route to one-step synthesis of trans-cyclooctene.

The preparative scale irradiations of cis-cyclooctene in pentane were run at concentrations of 0.12 and 0.6 M. A typical procedure is described for the photolysis of a 0.12 M solution since essentially the same procedure was employed with a 0.6 M solution. cis-Cyclooctene(5.0g, 0.045mol) and cycloheptane(0.1g) as an internal standard were dissolved in n-pentane(350 ml) and the solution was divided into five portions. Each portion(70ml) of the solution was successively placed in the immersion reactor, flused with nitrogen gas, and then irradiated for 6 hr without stirring. The irradiation period was determined by the glc analysis of aliquots removed from the reaction mixture. The combined irradiated solution(350ml) was concentrated to ca. 50 ml volume by distillation and extracted with five portions of 20% aqueous silver nitrate. The aqueous extracts were washed with two small portions of pentane and then added into ice-cooled concentrated ammonium hydroxide with vigorous stirring. The oily aqueous solution was extracted with three portions of pentane. The combined organic layers were washed with water, dried over magnesium sulfate, filtered, and the solvent

was removed by distillation under reduced pressure(50 torr). The product is trap-to-trap distilled under vacuum to give trans-cyclooctene; yield: 1.3 g(26% based on cis-cyclooctene used).

The ir and nmr spectra of this material were in good agreement with authentic trans-cyclooctene independently synthesized. Analysis on glc revealed that the product trans-cyclooctene contains only 0.4% of the cis-isomer as an impurity.

Independent syntheses of the authentic specimens.————— All compounds synthesized were identified by means of nmr, ir, and mass spectrometry.

Hepta-1,6-diene(2b) was synthesized by pyrolysis of heptamethylene glycol diacetate at 500°C according to the method of Marvel and Stille.[12] Octa-1,7-diene(2c) was commercially obtained. Nona-1,8-diene(2d) was synthesized by pyrolysis of nonamethylene glycol diacetate at 500°C according to the method of Marvel and Stille.[12]

Vinylcyclopentane(3b) was synthesized by a Wittig reaction of cyclopentanecarboxaldehyde.[13] Vinylcyclohexane(3c) was synthesized by pyrolysis of 2-cyclohexylethyl acetate, which was prepared by a Grignard reaction of ethylene oxide with cyclohexyl magnesium bromide[14] followed by esterification with acetyl chloride. Vinylcycloheptane(3d) was synthesized by pyrolysis of cis-cyclononene at 800°C.

Methylenecycloalkanes 4a-c were prepared by a Wittig reaction of the corresponding cycloalkanone, i.e. cyclopentanone, cyclohexanone, and cycloheptanone, according to similar procedures described in "Organic Syntheses".[15]

Bicyclo[n.1.0]alkanes(5)(n=3-6) were prepared by a Simmons-Smith reaction of the corresponding cycloalkenes with diiodomethane in the presence of zinc dust-copper(I) chloride mixture according to the method of Rawson and Harrison.[16]

Methoxycycloalkanes(6) were prepared by the reaction of the corresponding cycloalkanol with sodium hydride and the subsequent treatment with methyl iodide.

Results

Vapor-phase photolysis.————— The direct photolysis at 185 nm of cyclohexene 1a vapor gave ethylene and 1,3-butadiene as major decomposition products along with the rearrangement products, methylenecyclopentane(4a) and bicyclo-[3.1.0]hexane(5a). The yield of butadiene was virtually equal to that of

ethylene. The effect of cyclohexene pressure on the product yields was examined up to 30 torr in order to obtain informations on lifetime of the intermediate involved. The results are shown in Fig. 1. The effect of the pressure on suppress- ing yields of ethylene and butadi- ene is evident from the data, while the yields of the rearrangement pro- ducts 4a and 5a remain constant over the entire pressure range employed.

The products from the direct photolysis of cycloheptene 1b vapor was 1,6-heptadiene(2b), vinylcyclo- pentane(3b), methylenecyclohexane(4b), and bicyclo[4.1.0]heptane(5b).
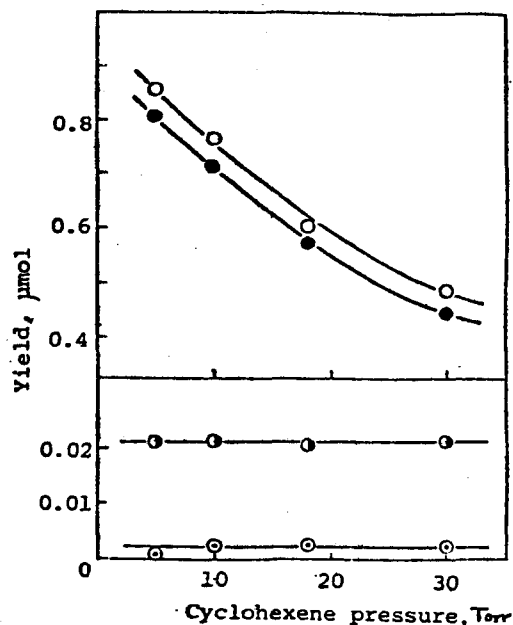

Figure 1   Product yield as a function of initial substrate pressure in vapor-phase photolysis of cyclohexene. Exposure time is 3 min: ○, ethylene; ●, butadiene; ◗, methylene- cyclopentane(4a); ◎, bicyclo[3.1.0]hexane(5a)

The pressure-dependence study was repeated. As shown in Table 1, the yields of heptadiene and vinylcyclopentane decrease with increasing cycloheptene pressure and those of methylenecyclohexane and bicycloheptane are practical- ly pressure-independent.

The direct photolyses of cis- and trans-cyclooctene vapor gave their cis-trans isomer, 1,7-octadiene(2c), vinylcyclohexane(3c), methylenecyclo- heptane(4c), and bicyclo[5.1.0]octane(5c). On increasing pressure by add- ing n-pentane as an inert gas, the yields of 2c and 3c were diminished, whilest the increase in the yield of the cis-trans isomer was observed; the yields of 4c and 5c were virtually invariant(see Table 2).

Table 1. Vapor-phase photolysis of cycloheptene 1b

Pressure	Exposure	Conversion	Product/µmol			
/torr	time/min	/%	2b	3b	4b	5b
3	3	1.6	0.105	0.181	0.038	a
9	3	0.43	0.062	0.120	0.033	0.008
15	3	0.22	0.049	0.097	0.034	0.008

a) Yield not determined.

Table 2.   Vapor-phase photolysis of cis- and trans-cyclooctene 1c

Pressure/torr					Product/µmol				
cis-1c	trans-1c	Pentane	Exposure time/min	Conversion /%	2c	3c	4c	5c	cis-trans Isomer
3	0	0	2	6.4	0.674	0.373	0.017	0.017	a
3	0	25	2	4.0	0.385	0.199	0.013	0.016	0.088
0	3	0	2	15.0	0.666	0.428	0.022	0.029	1.39
0	3	25	2	14.4	0.491	0.298	0.016	0.029	1.63

a) Formation not detected.

Table 3.   Liquid-phase photolysis of cycloalkenes 1a-c

Cycloalkene (0.01 M)	Exposure time/min	Conversion /%	Product/%[a]		
			2	3	cis-trans Isomer
Cyclohexene (1a)	30	31	22	43	-
Cycloheptene (1b)	30	30	34	27	-
cis-Cyclooctene (cis-1c)[b]	30	43	2.1	2.8	90
trans-Cyclooctene (trans-1c)[b]	30	44	2.1	3.6	84

a) Yield based on consumed cycloalkene.
b) Uncharacterized product (ca. 3%) was also observed.

Liquid-phase photolysis.──── The results of the direct photolysis at 185 nm of pentane solution containing 0.01 M cycloalkenes 1 are shown in Table 3.   In sharp contrast to the vapor-phase photolyses of these compounds, any formation of the decomposition products, α,ω-diene, or vinylcycloalkanes was not detected; the major photoproducts were only the rearrangement products, i.e. methylenecycloalkanes 4 and bicyclo[n.1.0]alkanes 5 (n=3-5), and the cis-trans isomer of 1c.

In order to clarify the formation mechanism of the rearrangement products, cycloheptene-1,2-d_2 (1b-d_2) was synthesized and subjected to the direct photolysis.   As shown in Table 4, the direct irradiation of pentane solution of 1b-d_2 gives a somewhat different product ratio from that obtained in the photolysis of non-deuterated cycloheptene under similar conditions. Any decrease in deuterium content was not observed with the products 4b and 5b on the analysis by gas chromatography-mass spectrometer combination.

Table 4.
   Liquid-phase photolysis of cycloheptene **1b** and its 1,2-d$_2$ isomer

Compound	Concentration /M	Exposure time/hr	Conversion /%	Product/%[a] 4b	5b	Ratio 4b/5b
1b	0.066	60	25	40	36	1.11
1b-d$_2$	0.066	60	38	38	38	1.0

a) Yield based on consumed substrate.

The product methylenecyclohexane-d$_2$ was separated gas-chromatographically from the irradiated solution of **1b-d$_2$**. The nmr spectrum of the compound in CCl$_4$ showed only the signals of four allylic protons at δ 2.05(m) and six methylene protons at 1.45(m), but the spectrum lacks the signal of olefinic protons, indicating the predominant deuteriation at the exo-methylene carbon of the methylenecyclohexane produced.

Direct photolysis in the presence of acidic methanol.————— Since, as described above, the liquid-phase photolysis of cis-cyclooctene gives its trans-isomer in good yield, it may be expected that cyclohexene and/or cycloheptene also photoisomerize into the highly strained trans-isomers upon direct irradiation, although the main course of the photolyses of these cycloalkenes is the rearrangement to methylenecycloalkanes and bicycloalkanes. However, the spectroscopic detection of these simple trans-isomers is difficult because of the probable absence of efficient uv absorption above 230 nm and the relatively low yield of the products. It is known in other system that trans-cyclohexene and trans-cycloheptene, and their 1-phenyl derivatives as well, react rapidly with acidic methanol forming the corresponding methyl ethers as an addition product. Hence, the direct photolyses of cyclohexene and cycloheptene were performed in the presence of acidic methanol in search of their highly strained trans-isomers. Unfortunately, methanol has an weak absorption band in the vacuum uv region and therefore the secondary reactions induced by the decomposition of methanol following photoexcitation will be unavoidable; the extinction coefficient at 185 nm of methanol is 140 1/mol·cm,[17] while those of the cycloalkenes are in the range of 5500-10000 1/mol·cm.[18]

The results of the direct photolyses of cyclohexene and cycloheptene in the presence of neutral methanol and acidic methanol are shown in Tables 5 and 6. The corresponding methyl ethers, i.e. methoxycyclohexane (**6a**) and

Table 5.
  Liquid-phase photolysis of cyclohexene **1a** in the presence of acidic methanol

Concentration/M			Exposure	Conversion	Product/%[a]		
1a	MeOH	H_2SO_4	time/min	/%	**4a**	**5a**	**6a**
0.01	0	0	30	31	22	43	b
0.01	0.50	0	30	49	9.0	20	0.7
0.01	0.50	0.03	30	46	9.6	22	4.4

a) Yield based on consumed cyclohexene.   b) Formation not detected.

Table 6.
  Liquid-phase photolysis of cycloheptene **1b** in the presence of acidic methanol

Concentration/M			Exposure	Conversion	Product/%[a]		
1b	MeOH	H_2SO_4	time/min	/%	**4b**	**5b**	**6b**
0.01	0	0	30	30	34	27	b
0.01	0.50	0	30	54	9.1	12	0.6
0.01	0.50	0.03	30	53	9.4	11	5.0

a) Yield based on consumed cycloheptene.   b) Formation not detected.

methoxycycloheptane(**6b**), were obtained in significant yields only on the
photolysis with acidic methanol.   Since the direct irradiation of methanol
is known to produce some radicals,[19] the increase of the conversion rate and
the decrease in the yields of the rearrangement products **4** and **5** may be at-
tributable to the subsequent radical-induced reactions which consume the
substrate alkenes.   Of course, the substrate cycloalkenes and the rear-
rangement products did not react with acidic methanol after standing for at
least one day under similar conditions. without uv irradiation.

Direct photolysis of cycloheptene at lower temperature.——— The direct ir-
radiation of pentane solution containing 0.01 M cycloheptene was carried
out for 3 hr in a dry ice-acetone bath.   The subsequent treatments after
the irradiation and the results are shown in Table 7.   It was revealed that
the precursor of methoxycycloheptane **6b** has an enough lifetime at -78°C to

Table 7. Liquid-phase photolysis of cycloheptene <u>1b</u> at -78°C

Treatment following the photolysis at -78°C	Conversion /%	Product/%[a]		
		<u>4b</u>	<u>5b</u>	<u>6b</u>
Warm (to room temperature)	9	23	24	b
Warm ——→ add acidic methanol	9	23	23	0.5
Add acidic methanol ——→ warm	9	25	24	4.7

a) Yield based on consumed cycloheptene. b) Formation not detected.

react with added acidic methanol after the cease of the irradiation. Even when acidic methanol was added after the above irradiated solution of cycloheptene has been allowed to stand for 20 hr at -78°C, the decrease in the yield of methoxycycloheptane was less than 20%.

The low-temperature experiment was repeated in order to determine the lifetime of trans-cycloheptene at lower temperature. The determination of the lifetime at -10°C of trans-cycloheptene was done by adding acidic methanol onto the aliquots removed from the irradiated

Figure 2   Logarithm of relative yield of methoxycycloheptane (<u>6b</u>) versus the time of standing for at -10°C.

solution which was kept at -10°C after the irradiation at -78°C.   The ligarithm of relative yields of methoxycycloheptane produced are plotted as a function of the time of standing for at -10°C in Fig. 2; a good linear relation was obtained, indicating the unimolecular decay of trans-cycloheptene.   The lifetime of trans-cycloheptene can be calculated from the data to be 23 min at -10°C.

Similar attempts with cyclohexene failed in the detection on glc of methoxycyclohexane suggesting the less stability of trans-cyclohexene at the temperature.

One-step synthesis of trans-cyclooctene by the direct irradiation of its cis-isomer.—— Upon direct photolysis of cis-cyclooctene in pentane, the
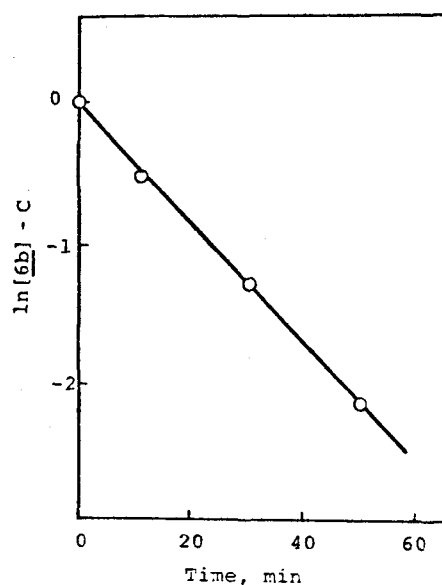
major photochemical reaction was the cis-trans isomerization as shown in Table 3, although the formation of small amounts of the rearrangement products 4c and 5c diminished the combined yield of cyclooctenes recovered. The yield of the product trans-cyclooctene increases with decreasing initial concentration of the cis-isomer, but the extreme dilution(to ~0.01 M) of the reaction mixture makes the efficient isolation and the preparation in gram quantity of the product difficult. With higher concentrations(>0.1 M), however, the yield of the trans-isomer was lower, partly because of the formation of any unknown product which may act as an internal filter and/or a sensitizer to prevent the reaction mixture reaching a 1:1 photostationary ratio(see Chapter 3). A practical procedure consists of the direct irradiation at 185 nm of a concentrated(0.12 or 0.6 M) solution of cis-cyclooctene and the subsequent extraction with aqueous silver nitrate; the yields are shown in Table 8. It is worth noting that the yields are satisfactorily high as compared with the other published photochemical preparations of this strained compound.[20]

Table 8.   Direct photolysis of cis-cyclooctene

cis-Cyclooctene concentration/M	Exposure time /hr	Yield of trans-cyclo- octene/%[a]
0.01	0.8	37[b]
0.12	6	26
0.6	10	12

a) Yield of isolated product, based on cis-cyclooctene used, unless otherwise noted.

b) Determined by glc.

Discussion

Vapor-phase photolysis.———— Two distinct mechanisms should be operative for the direct photolysis of cycloalkenes in the vapor phase, since apparent differences in the effects of pressure on the product yields are seen
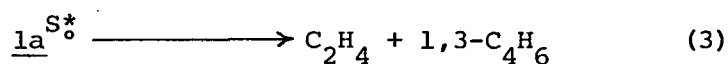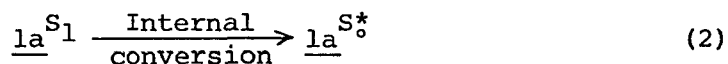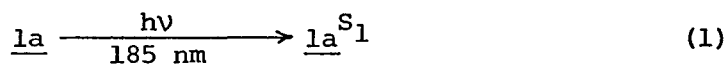
from the data shown in Fig. 1 and Tables 1 and 2. The products resulting from the vapor-phase photolysis of the cycloalkenes 1 may be classified according to the pressure dependence of their yields; the decomposition products, α,ω-dienes 2, and vinylcycloalkanes 3 are produced only on the vapor-phase photolysis and their yields decrease with increasing pressure, while the yields of the rearrangement products 4 and 5 are practically pressure-independent and these become the major photoproducts in the liquid-phase photolysis. The pressure effects observed depend intimately upon whether the precursor involved has a lifetime enough to suffer deactivating collision or the lifetime is too short to collide. Hence, the decomposition products, α,ω-dienes, and vinylcycloalkanes are inferred to be formed via an intermediate having relatively long lifetime. In other system,[1] it is known that with simple alkenes an electronically-excited singlet alkene undergoes rapid internal conversion into a vibrationally-activated ground state, and with molecules of this size the lifetime should be long enough to permit collisional deactivation of any energetic ground-state species which may be formed in an internal conversion process. Crandall and Watkins[21] reported that the vapor-phase pyrolyses of the cycloalkenes 1b-d gave the corresponding α,ω-dienes 2 and vinylcycloalkanes 3 as the major products. It is therefore concluded that the precursor of these pressure-dependent products is a vibrationally-excited ground-state cycloalkenes, which is produced via the internal conversion of the electronically-excited state generated initially by the direct irradiation. This conclusion is also supported by the observation that only the rearrangement products 4 and 5 are formed on the liquid-phase photolysis, in which excess vibrational energy is quickly removed by the collision with solvent molecules.

As described in Chapter 3, it was shown in the direct photolysis of 4,5-dimethylcyclohexene vapor that the decomposition of the cyclohexenes into cis- or trans-2-butene and butadiene undergoes via a short-lived allylic biradical on the basis of the partially non-stereospecific formation of 2-butene. It is also deduced that the intermediate of the decomposition products in the present photolysis of cyclohexene itself is a short-lived allylic biradical (7a)[22] produced by an allylic C-C bond cleavage of the vibrationally-activated cyclohexene. Similarly, the formation of the α,ω-dienes 2 and the vinylcycloalkanes 3 may be accounted for in terms of the competitive intramolecular disproportionation and recombination reaction of the analogous allylic biradicals 7b-d as shown in Scheme 1.
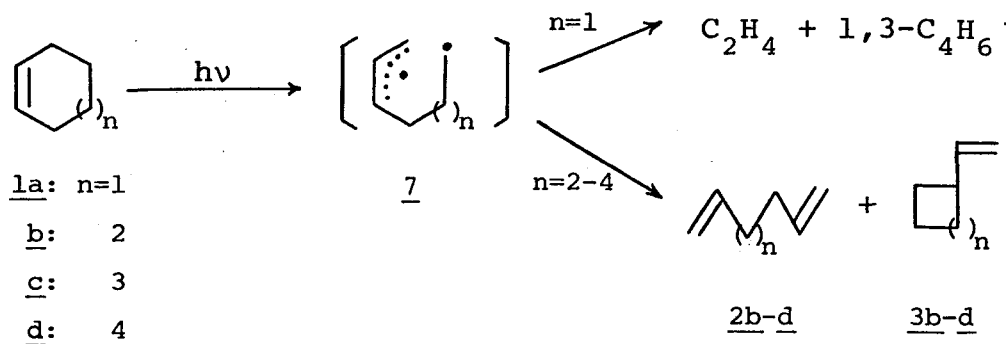
Scheme 1

A quantitative treatment of the pressure-dependence study on the photolysis of cyclohexene vapor gives additional information on the lifetime of the vibrationally-activated cyclohexene involved. The sequence 1-5 is proposed for the formation of ethylene and butadiene, the small amounts of the rearrangement products being neglected,

$$\underline{1a} \xrightarrow[\text{185 nm}]{h\nu} \underline{1a}^{S_1} \tag{1}$$

$$\underline{1a}^{S_1} \xrightarrow[\text{conversion}]{\text{Internal}} \underline{1a}^{S_o^*} \tag{2}$$

$$\underline{1a}^{S_o^*} \xrightarrow{\hspace{2cm}} C_2H_4 + 1,3-C_4H_6 \tag{3}$$

$$\xrightarrow{\hspace{2cm}} \underline{1a} \tag{4}$$

$$\xrightarrow[\hspace{2cm}]{\underline{1a}} \underline{1a} \tag{5}$$

where the superscripts S_1 and S_o^* represent the electronically-excited singlet and the vibrationally-activated ground states, respectively. A steady-state treatment of the sequence 1-5 leads to the equation 6 for the reciprocal of the yields of the products ethylene and butadiene.

$$1/\phi = \frac{k_3+k_4}{k_3} + \frac{k_5}{k_3}[\underline{1a}] \tag{6}$$

In Fig. 3, the reciprocals of the yields are plotted against the cyclohexene pressure and a good linear relation is obtained. From the slope and the intercept, the value $(k_3+k_4)/k_5$ is calculated to be 26.3 torr, for

the vapor-phase photolysis of cyclohexene. Assuming that the deactivation of the vibrationally-excited cyclohexene occurs at each collision, i.e. $k_5 = 1.0 \times 10^{-10}$ cc/molecule·sec, the value $k_3 + k_4$ is calculated to be 0.83×10^8 sec^{-1}. Thus the vibrationally-excited ground-state of cyclohexene has a lifetime of 1.2×10^{-8} sec.

The same treatment can be applied for the vapor-phase photolysis of cyclo-heptene, although only limited data are available with the pressure dependence of the product yields. The lifetime of the vibrationally-excited cyclo-heptene $\underline{1b}^{S*}_\circ$ can be estimated to be 3.3×10^{-8} sec by a similar calculation with the combined yield of heptadiene $\underline{2b}$ and vinylcyclopentane $\underline{3b}$.
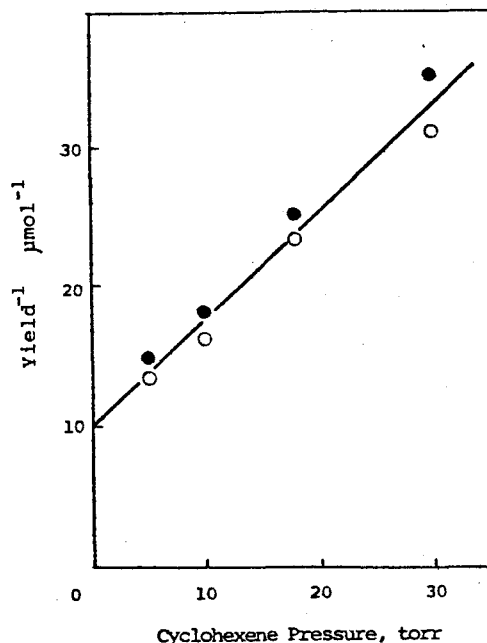

Figure 3 Reciprocal of yield of ethylene(○) and butadiene (●) as a function of pressure in vapor-phase photolysis of cyclohexene.

On the other hand, it is doubtless that the rearrangement products $\underline{4}$ and $\underline{5}$ are formed in pressure-independent process, probably from an electron-ically-excited state which has a lifetime short compared to the effective time between deactivating collisions even at higher pressures; the lifetime of the electronically-excited state involved may be around 10^{-10} sec. However the superposition near 185 nm of the R-N band over the continuum of the V-N band in the absorption spectra of the cycloalkenes complicates the situation. It cannot be concluded from the available data whether the electronically-excited state involved in the present photorearrangement is the excited singlet state or the π,R(3s) Rydberg(Ry) state of the cyclo-alkenes.[23] The detailed mechanism of this rearrangement reaction will be discussed below.

Liquid-phase photolysis.———— The direct photolyses of the cycloalkenes in the liquid phase give the rearrangement products and, when the trans-form is stable at room temperature, the predominant formation of the cis-trans isomer of $\underline{1c}$ is observed(Table 3). The formation of the steric isomer of $\underline{1c}$ is interpreted in terms of the photoisomerizaiton via the excited singlet state(see Chapter 3). The formation mechanism of these rearrangement products is of interest. The mechanism is inferred to involve the compet-ing rearrangements to $\underline{4}$ and $\underline{5}$ via the carbene intermediate which is produced

by the 1,2-shift of an allylic C-C bond of the excited cycloalkene(see Scheme 2).

Direct photolysis of the deuterated cycloheptene $\underline{1b}$-d$_2$ provides definitive evidences in support of the generation of the carbene $\underline{8b}$. The methylenecyclohexane-d$_2$ produced in the photolysis of $\underline{1b}$-d$_2$ carries its two deuteriums only on the exo-methylene carbon, supporting the mechanism involving the hydrogen(deuterium) transfer to the carbene center in the intermediate $\underline{8b}$.

$\underline{1b}$ $\underline{8b}$ $\underline{4b}$ $\underline{5b}$
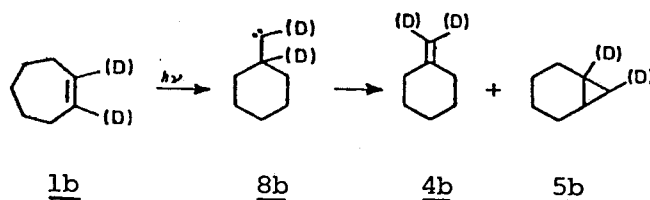
Scheme   2

Furthermore, the photolysis of $\underline{1b}$-d$_2$ gives a somewhat different product distribution from that obtained in the photolysis of non-deuterated cycloheptene as shown in Table 4. The decrease in yield of $\underline{4b}$ and the increasing in yield of $\underline{5b}$ can be explained in terms of the competing hydrogen transfer and insertion to C-H bond of the carbene $\underline{8b}$, since the deuteration at the 1- and 2-positions of $\underline{1b}$ causes the rate of the hydrogen transfer in the carbene to be slow, leading to the decrease in the yield of $\underline{4b}$-d$_2$. Assuming that the rate of the intramolecular insertion of the carbene $\underline{8b}$ to C-H bond is not affected by the deuteration, the isotope effect on the hydrogen transfer process in the carbene, denoted by k_H/k_D, is calculated to be 1.11; the value should be compared with the isotope effect, k_H/k_D= 1.12, observed for the transfer of a tertiary hydrogen in isopropylcarbene which is generated by the photolysis of the corresponding diazoalkane.[24] Likewise, the postulation of analogous carbenes $\underline{8a}$ and $\underline{8c}$ is also recognized in the photolysis of the other cycloalkenes $\underline{1a}$ and $\underline{1c}$ as the precursor of the rearrangement products $\underline{4}$ and $\underline{5}$.

Highly strained trans-cycloalkenes.———— The efficient photochemical conversion to trans-cyclooctene of its cis-isomer prompt to the search for highly strained trans-isomers of the smaller-sized cycloalkenes $\underline{1a}$ and $\underline{1b}$ in the liquid-phase photolysis. Since spectroscopic detection of these trans-isomers is difficult for lack of effective absorption in an accesible

uv region, chemical trapping of trans-cyclohexene and trans-cycloheptene by acidic methanol was applied on the liquid-phase photolysis of their cis-isomers. As shown in Tables 5 and 6, methoxycycloalkanes 6a and 6b are obtained in significant yields only on the photolysis with acidic methanol, although the introduction of methanol to the reaction system reduces the yields of the rearrangement products 4 and 5.

While the addition products with methanol are obtained on the direct photolysis of the cycloalkenes 1a and 1b in the coexistence of the trapping agent, it may remain uncertain whether the precursor of these adducts is really the ground-state trans-isomers or, with minor possibility, the electronically-excited state of the alkene itself. A further support of the formation of trans-cycloheptene in its ground state comes from the direct photolysis of cis-cycloheptene at lower temperature and the subsequent addition onto the irradiated solution of acidic methanol after the cease of the irradiation(see Table 7). Considerable amount of methoxycycloheptane 6b is obtained even when acidic methanol is added after standing the irradiated solution for 20 hr at -78°C. It is obvious that the precursor of methoxycycloheptane is the highly strained trans-cycloheptene and has an enough lifetime at -78°C to react with added acidic methanol after the cease of the irradiation. The lifetime of trans-cycloheptene is calculated to be 23 min at -10°C. This may be the first evidence which indicates the formation and the trapping of trans-cycloheptene in its ground state.

The reactions of cycloalkenes following direct excitation at 185 nm are summarized in Scheme 3.
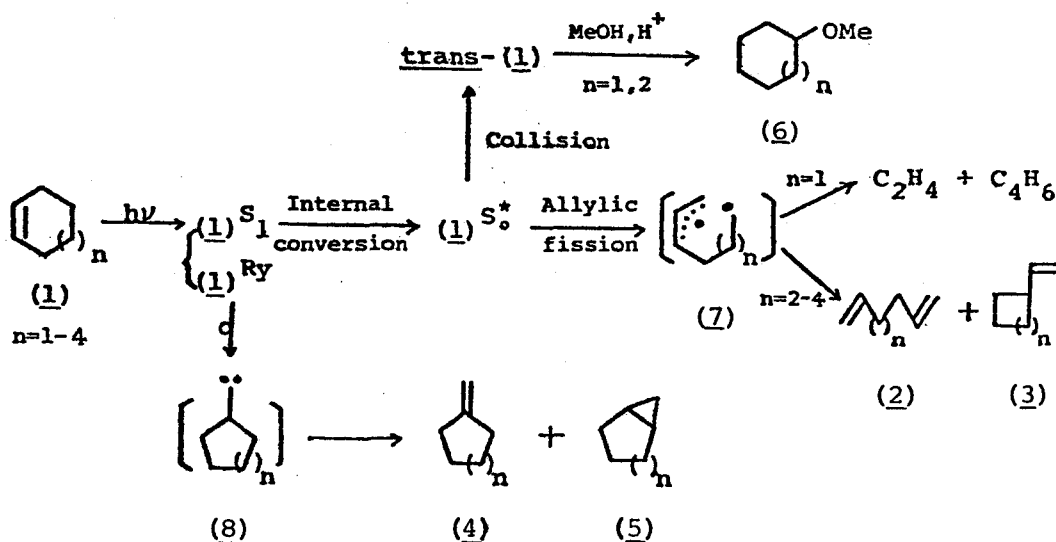
Scheme 3

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22) The intermediate allylic biradical will be proved in Chapter 3.

23) Recently, Kropp et al.[3] have reported that tetrasubstituted alkenes, e.g. 2,3-dimethyl-2-butene, undergo a similar photorearrangement involving a carbene intermediate, probably via a Rydberg state, on direct irradiation at > 220 nm. Although they observed the photorearrangement of several tetrasubstituted alkenes to carbene-derived products, similar behavior of di- or tri-substituted alkenes has not been known. In a preliminary experiments of the auther on the benzoate photosensitization of simple alk-enes, it is shown that methyl benzoate acts as a singlet sensitizer to generate an excited singlet state of alkene, probably via a singlet exciplex. On the basis of the fact, in the benzoate sensitization of cyclooctene 1c, only the cis-trans isomerization occurs without the photorearrangement to the carbene-derived products 4c and 5c, the excited state involved in the present photorearrangement may be inferred to be the Rydberg excited state of the cycloalkenes 1.

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Chapter 2   Sensitized Photolysis of Simple Alkenes:

Intramolecular Hydrogen Transfer of Vibrationally
Excited π,π^* Triplet State

2-1   Triplet Sensitization of Cycloalkene Vapor

Extensive studies have been made on the photochemical behavior of alkyl-substituted ethylenes following triplet sensitization in the liquid phase. The cis-trans photoisomerization of acyclic alkenes via triplet state is one of the most studied photochemical reactions;[1] with cycloalkenes, where cis-trans isomerization is geometrically difficult, cyclodimerization and polar addition take place.[2] Regarding the photosensitization of simple alkenes in the vapor phase, on the other hand, it is generally accepted that triplet-triplet energy transfer from sensitizer generates a vibrationally excited triplet-state molecule of alkene, which exhibits some reactivities not observed in the liquid-phase photolysis. The best established reaction of such a vibrationally excited triplet alkene is allylic C-C and C-H bond cleavage followed by reactions of the resulting alkyl and allyl radicals.[3-8] However, work on the vapor-phase photosensitization so far reported has placed emphasis on the decomposition reactions of lower molecular-weight alkenes ($\sim C_6$) mainly because of their higher vapor pressure available; no systematic survey for the reaction of such a vibrationally excited triplet alkene of higher molecular weight has been made.

In this section, some novel behaviors, which are peculiar to the vibrationally excited triplet state of cycloalkenes (C_7-C_9), and their detailed mechanisms will be discussed.

Experimental

<u>Materials.</u>——— cis-Cyclooctene-5,6-d_2.   To a stirred solution containing cycloocta-1,5-diene (25 g, 0.23 mol) in CCl_4 (150 ml) at -10°C was added drop-wise bromine (33.3 g, 0.21 mol) in CCl_4 (50 ml).   On removal of the solvent and the excess of diene, an oily residue was obtained which when fractionated under reduced pressure gave 5,6-dibromocyclooctene (27 g, 44%), b.p. 91 -95°C at 1.0 torr, nmr (CCl_4) δ 5.7 (2H, br. s), 4.65 (2H, s), and 1.8-3.0 (8H, m).   Reduction of the dibromide (25 g, 0.093 mol) was conducted with a

mixture of $LiAlD_4$ (1.0 g, 0.024 mol;Merck) and LiD(2.5 g, 0.31 mol;Merck) in tetrahydrofuran under reflux. Basic work-up[9] gave a mixture(7.1 g), b.p. 140-150°C at 760 torr, composed mainly of cyclooctene-5,6-d_2 (27%) and cyclo-octa-1,5-diene(65%). Separation by preparative glc on a PEG column afforded the labelled cyclooctene containing 1.1% bicyclo[5.1.0]octane **3**, 0.2% cyclo-octane, and 0.05% bicyclo[3.3.0]octane **5**. The ir spectrum of the deuterated compound showed an absorption at 2180 cm^{-1} attributable to C-D stretching. The isotopic purity(98.9%) was confirmed by nmr and mass spectrometry.

Quantitative Photolyses.———— All experiments were carried out at room temperature and under static conditions. Mercury photosensitization in the vapor phase was conducted using cylidrical quartz cells, 5 cm long and 5 cm in diameter, and a conventional vacuum system. A mercury-free vacuum system and similar cylindrical cells were used for benzene photosensitization in the vapor phase. Both sensitizations were performed using a spiral array of 30 W low-pressure mercury lamps fitted with a Toshiba UV-25 filter. The lamp was allowed to warm up for at least 30 min before each run in order to reach a stable operating condition. A control run revealed that no detectable reaction occurred in the absence of uv irradiation. The quantum yield(ϕ) for mercury sensitization was determined by propane actinometry at 300 torr, where $\phi(H_2)$ was taken as unity.[10] The absorption of the incident radiation was incomplete in the cell and appropriate corrections were made in the determination of the quantum yields.

After each run, products were trapped in a capillary at -196°C. The non-condensable products were analyzed and measured by a combination of Toepler pump, gas burette, and Pd-chamber. The condensables were analyzed by glc on a 9 m column of 20% polyethylene glycol-6000(PEG) or a 6 m column of 20% β,β'-oxydipropionitrile(ODPN). All products, which can be separated cleanly from each other under these conditions, had retention times identical with those of authentic specimens on glc employing ODPN, PEG, and dinonyl phthalate columns. Analysis of dimeric products from the mercury sensitiza-tion was performed by glc on a 1.5 m FFAP column at 150°C. The molecular weights of the dimers were measured using a Hitachi RMS-4 glc-mass spectro-meter combination.

Preparative Photolyses.———— The preparative scale mercury-sensitized photo-lysis of cis-cyclooctene **1c** was carried out at its b.p. at atmospheric pressure. A cylindrical quartz cell, 20 cm long and 2 cm in diameter, was mounted vertically along the axis of a helical array of 30 W low-pressure mercury lamp. The lower end of the cell, where an externally heated tray

containing mercury(ca. 1g) was interposed, was connected to a flask in which 1c(70 g), with hydroquinone(1 g) as an inhibitor, was placed. The top end of the cell was attached to a reflux condenser. On heating the contents of the flask, the vapor of the substrate and mercury ascended the cell, condensed at the surface at the top, and dropped back into the flask. The heat from the lamp prevents any condensation on the wall of the cell. After irradiation for 80 hr, the contents of the flask were fractionated through a spinning band column to give a fraction(18.6 g), b.p. 120-145°C at 760 torr. Isolation of the products was performed by preparative glc on PEG. The nmr and mass spectra of the products agreed exactly with those of authentic specimens which were either commercial(1,7-octadiene) or independently synthesized.

The mercury photosensitization of cis-cyclononene with 10% nitric oxide was carried out at the pressure of 1.5 torr for 12 hr using the 30 W mercury lamp and a preparative irradiation apparatus which was made up of a 5 l Pyrex vessel, two quartz cells for irradiation, and a thermosiphone for circulation of the gas. Isolation of the products was performed by preparative glc. The nmr and mass spectra of the products separated above made the identification certain.

Independent synthesis of authentic specimens.——— Bicyclo[4.2.0]octane(4) was synthesized by photocyclization of 1,3-cyclooctadiene to bicyclo[4.2.0]oct-7-ene[11] and subsequent hydrogenation of the bicyclooctene to 4 over platinum.

Bicyclo[3.3.0]octane(5) was synthesized by potassium catalyzed cyclization of 1,3-cyclooctadiene to bicyclo[3.3.0]oct-2-ene[12] and subsequent hydrogenation over platinum.

cis-Bicyclo[4.3.0]nonane was prepared by hydrogenation of indene over Raney nickel W-2 at 180°C for 3 hr at the hydrogen pressure of 200 atm in an autoclave.

trans-Bicyclo[4.3.0]nonane was prepared by acetone-sensitized photo-epimerization of its cis-isomer.[13]

Result

Mercury-sensitized photolysis of cycloheptene.——— Cycloheptene(6 torr) vapor was irradiated with a low pressure mercury lamp in the presence of mercury vapor at room temperature to give bicyclo[4.1.0]heptane(ϕ=0.088), vinylcyclopentane(0.054), and 1,6-heptadiene(0.025); hydrogen, ethylene,

and 1,4-pentadiene were also observed as minor products.

Mercury-sensitized photolysis of cis-cyclooctene.————— The major products of the mercury photosensitization of 1c were hydrogen, ethylene, 1,5-hexadiene, 1,7-octadiene(2), bicyclo[5.1.0]octane(3), bicyclo[4.2.0]octane(4), and trans-cyclooctene(1t). The quantum yields of the products are shown in Table 1. The yield of hexadiene equals that of ethylene. Although a search was made for cyclooctane and dimeric C_{16} compounds which are familiar radical products in mercury photosensitization of alkanes,[3] these were not observed in significant yields(ϕ< 0.02). Glc-mass spectrometric analysis showed that the dimeric products were composed of $C_{16}H_{26}$, $C_{16}H_{28}$, and $C_{16}H_{30}$, which may correspond to bicyclooctenyl, cyclooctylcyclooctene, and bicyclooctyl, respectively. The fragmentation pattern of the mass spectra suggested the absence of cyclic dimers with a cyclobutane ring.

The product distribution for a short reaction time(1 min) was in good agreement with the results shown in Table 1, thus indicating that these are the primary photoproducts.

An experiment was performed with a small amount of nitric oxide added as a radical scavenger since radical-induced reactions caused by excited mercury atoms are well known in mercury photosensitization of hydrocarbons.[3] As is shown in Table 1, the yields of the major photoproducts were not affected by the addition of nitric oxide.

The effect of pressure on the product yields was examined up to 150 torr by adding carbon dioxide as an inert gas since the range available was limited by the low vapor pressure(ca. 6 torr) of the substrate at room temperature. The effect of the pressure on suppressing product yields is evident from the data shown in Fig 1.

TABLE 1
Sensitised photolysis of (1c)

Sensitiser	p/Torr (1c)	NO	Exposure time/min	(2)	(3)	(4)	(5)	(1t)	Hexadiene	C_2H_4	H_2
Mercury [a]	4.5	0	3.0	0.181	0.049	0.128	0.025	0.075	0.017	0.019	0.017
	4.5	0.5	3.0	0.191	0.049	0.129	0.025	0.074	0.018	c	c
Benzene [b]	5.0	0	15.0	0.010	d	0.006	d	0.107	0.001	c	d

[a] Yields shown as ϕ. [b] 5 Torr benzene added as sensitiser. Yields shown in μmol. [c] Not determined. [d] Not detected.

TABLE 2
Mercury photosensitisation of (1c) and its [5,6-$^2H_2$] isomer

Compound	p/Torr	Exposure time/min	(2)	(3)	(4)	(5)	(1t)	Hexadiene	C_2H_4
(1c)	4.0	4.0	0.812	0.311	0.578	0.109	0.538	0.013	0.013
[5,6-$^2H_2$]-(1c)	4.0	4.0	0.744	0.401	0.541	0.092	0.666	0.009	0.010

[a] Average of four independent runs.
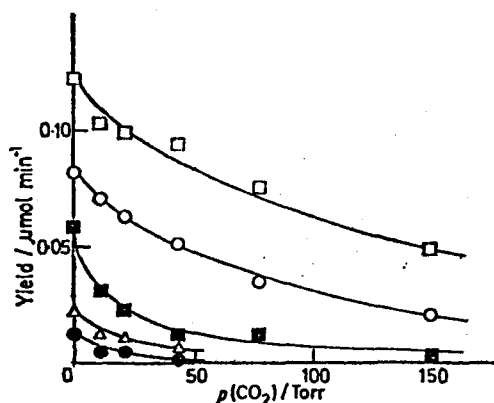
FIGURE 1 Product yield as a function of added CO_2 pressure in the mercury sensitisation of (1c). The pressure of the substrate is 3.0 Torr: (2), □; (3), ■; (4), O; (5), △; (1t), ●.
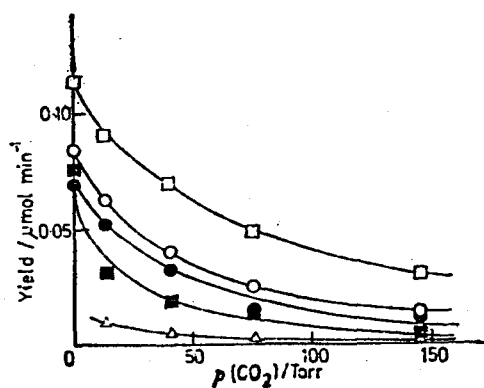
FIGURE 2 Product yield as a function of added CO_2 pressure in the mercury sensitisation of [5,6-$^2H_2$]-(1c). The pressure of the substrate is 3.0 Torr: (2), □; (3), ■; (4), O; (5), △; (1t), ●

Since the formation of 4 and 5 was considered to involve hydrogen transfer at the 5- and 6-position of 1c, cyclooctene-5,6-d_2 was synthesized and subjected to mercury sensitization in order to examine isotope effects on the reaction. The reaction was carried out under comparable conditions, and afforded similar results except for somewhat different distribution of the products, as shown in Table 2. Any detectable decreases in deuterium content were not observed by mass spectrometry of the products 2-5 and 1t. Mass spectrometric analysis also revealed that at least 80% of the hexadiene produced contains two deuterium atoms, suggesting predominant elimination of ethylene-d_0.

The study of the effect of pressure was repeated for the mercury sensitization of the deuterated cyclooctene with added carbon dioxide under comparable conditions, since deuteration at the 5- and 6-position of 1c is expected to affect the rate of hydrogen transfer. As shown in Fig. 2, the product yields decrease with increasing pressure as in the case of 1c except for greater reduction of the yields of 2 and 4.

In a separate experiment, mercury photosensitization of trans-cyclooctene 1t under similar conditions gave analogous products, i.e. hydrogen, ethylene, 1,5-hexadiene, 2-5, and 1c with a different distribution of the products. A control run, however, revealed that the substrate suffers isomerization to a limited extent(ca. 3%) to the cis-isomer in the absence of irradiation. Therefore, some uncertainty in the determination of the yield of 1t is unavoidable in the photolysis of 1c

Benzene-sensitized photolysis of cis-cyclooctene.———— Vapor-phase photolysis of 1c was examined with benzene vapor as sensitizer using a mercury-

free vacuum system. As shown in Table 1, benzene sensitization of 1c afforded mainly 1t along with 2, 4, and trace amounts of ethylene and 1,5-hexadiene. It is noteworthy that except for 1t benzene sensitization gave only two of the isomeric products obtained by mercury sensitization.

Liquid-phase photolysis of 1c was attempted with benzene or xylene as a sensitizer to give 1t as sole product in agreement with the literature.[14] Analysis by glc showed the absence of peaks corresponding to isomers 2-5.

Sensitized photolysis of cis-cyclononene.———— In sensitized photolysis of cis-cyclononene, mercury and benzene vapor were used as the sensitizer. The products of the photosensitization were 1,8-nonadiene, cis- and trans-bicyclo[4.3.0]nonanes, cis- and trans-bicyclo[5.2.0]nonanes, and cis-bicyclo-[6.1.0]nonane, as shown in Table 3.

TABLE 3. PHOTOLYSES OF cis-CYCLONONENE(1c)

| Photolysis mode	Pressure, Torr	Exposure time, min	Product, μmol							
			⋀⋁⋀⋀	⬡＾	⬡⬡	⬡⬡	⬡□	⬡□	⬡▷	H₂
Mercury-sensitization	1.0	2.0	0.07	o	0.11	0.12	0.54	1.18		0.04
Benzene-sensitization	1.0	30	0.05	o	0.23	0.08	0.02	0.02		o

Discussion

It is generally accepted that a primary process between an excited mercury atom(6^3P_1) and an alkene molecule leads to a vibrationally excited triplet state of the alkene.[3] In the present system, the pressure dependence of the product yields and the lack of ihibition by nitric oxide indicated the formation of a vibrationally excited cycloalkene triplet; this is consistent with the accepted view on alkene photochemistry.

In mercury sensitization of cycloheptene, the formation mechanism of bicyclo[4.1.0]heptane is of interest, since the mercury photosensitized cyclization of alkene to cyclopropane derivative has been observed in some cases.[4,15] There, however, are some mechanistic uncertainties with the

formation of cyclopropane derivatives, since the following alternative paths may be considered; 1) a 1,2-shift of an allylic hydrogen atom(concerted or stepwise), 2) a $(2\pi+2\sigma)$ intramolecular cycloaddition reaction well-known in the photocyclization of cycloalkenones in solution.[16] Although the mechanism may differ in each cases, it is worthwhile to reveal the formation mechanism of bicyclo[4.1.0]heptane. To the purpose, cycloheptene-1,2-d_2 was synthesized and photolyzed using a preparative irradiation apparatus of 5 l volume.
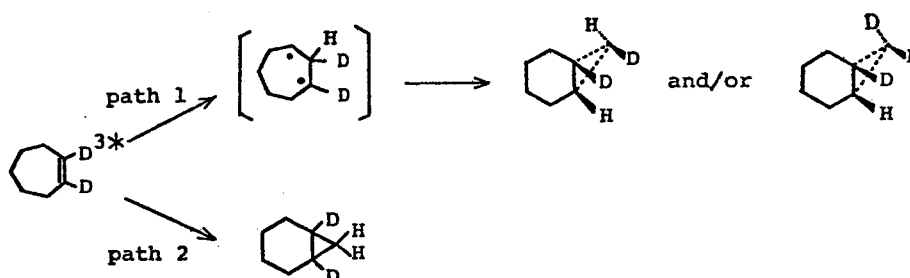

Then the bicyclo[4.1.0]heptane-d_2 was separated by preparative glc from the photolyzate.[17] The nmr spectrum in $CDCl_3$ showed the signals of the bridgehead proton at ca. δ 0.9(m), 7-exo-proton at ca. 0.5(m), and 7-endo-proton at -0.02(br. s) with their ratio of 2:1:1, indicating that the resulting bicycloheptane contains its one deuterium on 7-exo and 7-endo-carbon in the ratio of 1:1. Therefore, it is concluded that the bicycloheptane is formed via the stepwise path composed of 1,2-hydrogen shift followed by 1,3-closure of the resulting biradical(stepwise path 1).

On mercury photosensitization, cyclooctene triplet formed underwent unique isomerization reactions to give three bicyclooctanes 3-5 in contrast to other alkene triplets generated by mercury photosensitization, which have hitherto been reported to undergo allylic C-C and/or C-H bond cleavage.[3] The lack of inhibition by nitric oxide indicates that the formation of the bicyclooctanes cannot be explained in terms of a radical-initiated cyclization, as exemplified for bicyclo[3.3.0]octane.
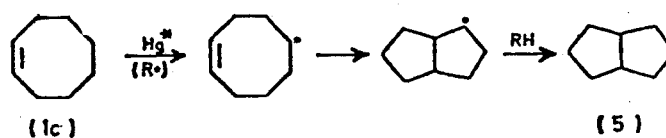
Bicyclo[5.1.0]octane 3 is probably formed via a 1,2-shift of an allylic hydrogen atom as in the formation of bicyclo[4.1.0]heptane in the photolysis of cycloheptene. The mechanism of formation of the other bicyclooctanes also involves intramolecular hydrogen-transfer processes followed by closure of the resulting cyclic biradicals(Scheme 1).[18]
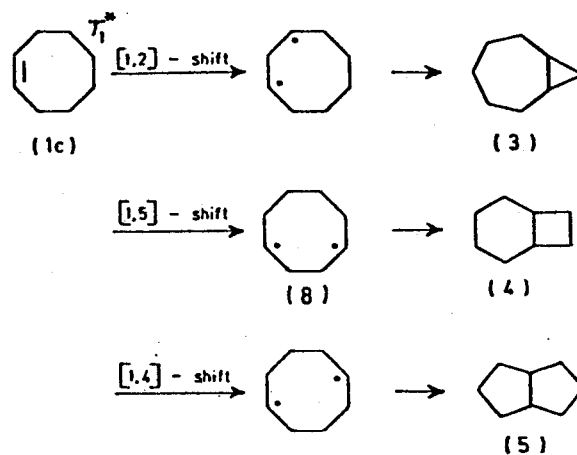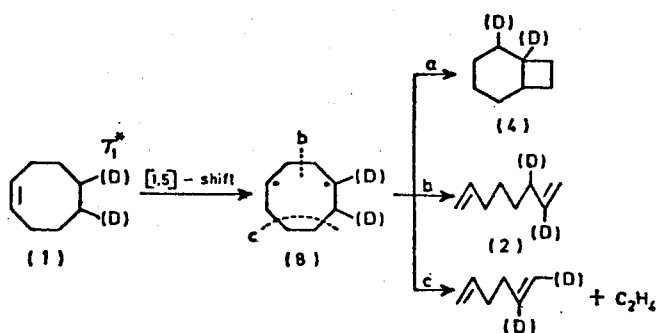

SCHEME 1

On the other hand, the α,ω-dienes might result from intramolecular disproportionation of the allylic biradicals 6 and 7 produced by the familiar allylic C-C cleavage(Scheme 2).
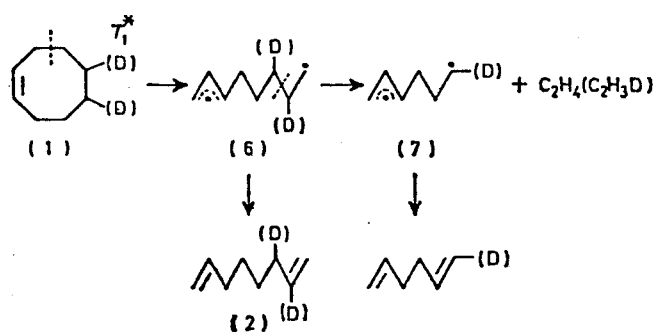
SCHEME 2

There are, however, some mechanistic ambiguities in the formation of the α,ω-diene, since it cannot be reasonably explained why allylic biradicals such as 6 and 7 undergo intramolecular disproportionation preferentially to form α,ω-dienes without giving the more stable conjugated 1,3-dienes. Furthermore, it is difficult to rule out the possibility that the biradical 7 cyclizes to cyclohexene and/or vinylcyclobutane.[19]
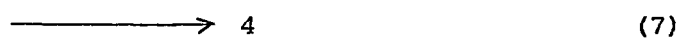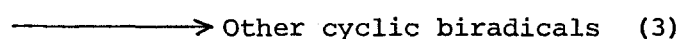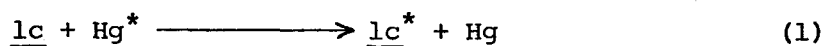
SCHEME 3

As an alternative mechanism for the formation of α,ω-dienes, the intervention of the cyclic 1,4-biradical 8, which was proposed as a precursor of 4 may be considered(Scheme 3). β-Cleavage of such a 1,4-biradical is a well known reaction.[20] The most remarkable feature of the mechanism is that the resulting dienes should be exclusively terminal. If the cyclic biradical 8 undergoes elimination of ethylene yielding an equimolar amount of 1,5-hexadiene(path c in Scheme 3), the allylic biradical 6 in Scheme 2 may also be ruled out as the precursor of the decomposition products. Since the position from which ethylene molecule is eliminated in 1c is different in the intermediates 6 and 8, the two mechanisms are clearly distinguishable by the deuterium labelling at the 5- and 6-positions of 1c as illustrated in Schemes 2 and 3. Photolysis of cis-cyclooctene-5,6-d_2 gave hexadiene, for which mass spectrometric analysis revealed the presence of >80% 1,5-hexadiene-d_2.[21] It is concluded that most of the ethylene is attributable to molecular elimination from 8, and this may be considered as evidence in support of path b in Scheme 3 for the formation of octadiene 2, which is more reasonable than Scheme 2.

However, it remains unanswered whether the formation of the octadiene 2 via the allylic biradical 6 is thoroughly ruled out. One might suppose that the octadiene was attributable to both the allylic biradical 6(Scheme 2) and the cyclic biradical 8(Scheme 3). A study of the kinetics of the photolysis of 1c and the 5,6-d_2 isomer will provide further evidence on the mechanisms of formation of the octadiene. Deuterium substitution at the 5- and 6-positions of 1c is expected to cause a marked decrease in the rate of hydrogen transfer from these positions and, therefore, in the rate of the formation of bicyclo[4.2.0]octane 4. On the other hand, the rate of formation of the octadiene 2 formed via the allylic biradical would not be affected by deuterium labelling, since the rate-determining step is probably the fission of allylic C-C bond. Therefore, if some octadiene was formed via the allylic biradical, a smaller isotope effect would be observed in

the formation of octadiene compared with that of bicyclo[4.2.0]octane. The sequence 1-7 is proposed for the formation of $\underline{2}$ and $\underline{4}$, the small amount of decomposition of $\underline{1c}$ and quenching of excited mercury by CO_2 being neglected. 'Other cyclic diradicals' include the cyclic 1,3- and 1,5-species shown in Scheme 1; the asterisk represents the excited triplet state.

$$\underline{1c} + Hg^* \longrightarrow \underline{1c}^* + Hg \qquad (1)$$

$$\underline{1c}^* \longrightarrow \underline{8} \qquad (2)$$

$$\longrightarrow \text{Other cyclic biradicals} \qquad (3)$$

$$\overset{\underline{1c}}{\longrightarrow} \underline{1c} \qquad (4)$$

$$\overset{CO_2}{\longrightarrow} \underline{1c} \qquad (5)$$

$$\underline{8} \longrightarrow \underline{2} \qquad (6)$$

$$\longrightarrow \underline{4} \qquad (7)$$

A steady-state treatment of sequence 1-7 results in equation 8 for the reciprocal of quantum yield of the biradical $\underline{8}$ versus CO_2 pressure, and 9 and 10 for those of $\underline{2}$ and $\underline{4}$.

$$1/\phi_{\underline{8}} = 1 + k_3/k_2 + k_4[\underline{1c}]/k_2 + k_5[CO_2]/k_2 \qquad (8)$$

$$1/\phi_{\underline{2}} = (1 + k_7/k_6)(1/\phi_{\underline{8}}) \qquad (9)$$

$$1/\phi_{\underline{4}} = (1 + k_6/k_7)(1/\phi_{\underline{8}}) \qquad (10)$$

In Figs. 3(a) and (b), the reciprocals of yields of $\underline{2}$ and $\underline{4}$ from the photolysis of $\underline{1c}$ and the 5,6-d_2 isomer are plotted against CO_2 pressure and good linear relations are obtained. Assuming that the value k_6/k_7 for both $\underline{1c}$ and the 5,6-d_2 isomer to be identical, the isotope effect on the rate of process 2, denoted by $'k_H/k_D'$,[22] is estimated from the slopes of both equations 9 and 10. From Figs. 3(a) and (b) the value of $'k_H/k_D'$ for the

formation of $\underline{2}$ is 1.67 and for $\underline{4}$ is 1.70; these values are in good agreement. Despite the negligible difference in the quantum yield $(\phi_H/\phi_D$ in Table 4), the rates of formation of $\underline{2}$ and $\underline{4}$ decreased to a similar extent upon deuteration, which is consistent with a mechanism involving intramolecular hydrogen transfer. This supports the presence of biradical $\underline{8}$ as a common intermediate for $\underline{2}$ and $\underline{4}$ and in consequence indicates the absence of the allylic biradical $\underline{6}$.

TABLE 4

Isotope effects on the quantum yield and the rate constant in the photolysis of (1c) and its [5,6-^{2}H$_2$] isomer

Product	ϕ_H/ϕ_D *	$'k_H/k_D'$
(2)	1.09	1.67
(4)	1.07	1.70

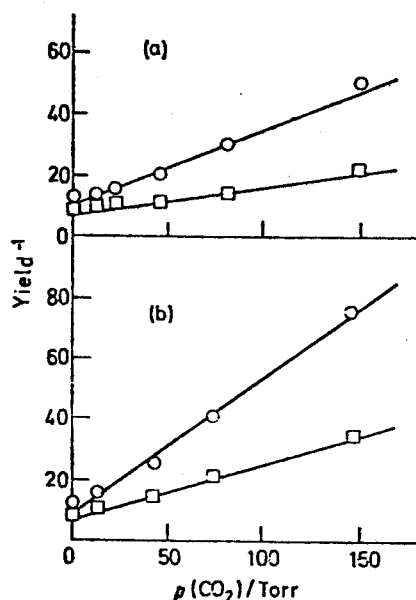* Calculated from the value shown in Table 2.

FIGURE 3 Reciprocal of yield *versus* added CO$_2$ pressure in the mercury sensitisation of (a) (1c) and (b) [5,6-^{2}H$_2$]-(1c): (2), □; (4), O

Since the products $\underline{2}$, $\underline{4}$, and hexadiene are formed via $\underline{8}$, the most important primary process in the mercury sensitization of $\underline{1c}$ is considered to be a transannular 1,5-shift of hydrogen which occurs through a six-membered transition state whose quantum yield calculated from those of $\underline{2}$, $\underline{4}$, and hexadiene is 0.33(see Table 1). Bicyclo[3.3.0]octane $\underline{5}$ formed from a 1,4-hydrogen shift via an unfavorable five-membered transition state is only a minor product. Intramolecular hydrogen abstraction in the six-membered transition state, followed by competitive cyclization and β-cleavage of the resulting 1,4-biradical, corresponds to the well known γ-hydrogen abstraction observed in the photolysis of carbonyl compounds.[23] This may be the first reported case in which a π,π^* triplet of a simple alkene undergoes a Norrish type II reaction.[24] The sensitized photolysis of $\underline{1c}$ in solution afforded only $\underline{1t}$, and the intermediate in the photoisomerization

is believed to be the <u>vibrationally</u> <u>relaxed</u> π,π^* triplet which never gives bicyclooctanes. On the other hand, it is considered that the π,π^* triplet generated in mercury sensitization is in a <u>vibrationally</u> <u>excited</u> state and is much more slowly deactivated by collision in the vapor phase. Vibrational activation in the triplet state enhances the rate of the novel hydrogen abstraction reaction.

Although it is suggested that the excess vibrational energy of the triplet state plays a significant role in mercury sensitization, its effect on the reactivity of the triplet remains unclear.

Benzene sensitization in th vapor phase[25] is expected to give a triplet having lower vibrational energy whose reactivity is of interest. Photolysis of <u>1c</u> in the presence of benzene vapor gave mainly <u>1t</u> together with <u>2</u>, <u>4</u>, and trace amounts of hexadiene and ethylene. The formation of <u>1t</u> suggests the intermediacy of the cyclooctene triplet resulting from the energy transfer from the benzene triplet. This cyclooctene triplet afforded only two of the isomeric products obtained by mercury sensitization. These products, <u>2</u> and <u>4</u>, are also considered to arise from the Norrish type II-like reaction proposed in Scheme 3. The other possible hydrogen shifts, i.e. 1,4- and 1,2-, which occurred in mercury sensitization, were not observed. This result is explained on the basis that only the energetically favored path, the 1,5-shift, takes place, since the triplet formed in benzene sensitization has less vibrational energy than that from mercury sensitization by the difference in the triplet energy of the sensitizer, 84 and 113 kcal/mol, respectively.

The marked difference in the product distribution between the mercury and benzene sensitization of cis-cyclononene is also attributable to the different triplet energies of the sensitizers. Since the benzene sensization of cis-cyclononene in the liquid phase did not afford any of these products, it is considered that the intermediate involved in the vapor-phase photosensitization is a vibrationally excited triplet of cis-cyclononene and that the vibrational activation in the triplet state enhances the photorearrangement. Similarly to the mechanism shown in the bicyclo[4.1.0]heptane formation in the mercury photosensitization of cycloheptene, the formation of cis-bicyclo[6.1.0]nonane is interpreted in terms of a 1,2-shift of allylic hydrogen followed by the ring closure of the resulting 1,3-biradical(Scheme 4). The intramolecular hydrogen abstractions by the excited C=C double bond via two possible six-membered transition states give cyclic 1,4- and 1,6-biradicals, and the subsequent β-cleavage or recombination of the resulting biradicals leads to the products.
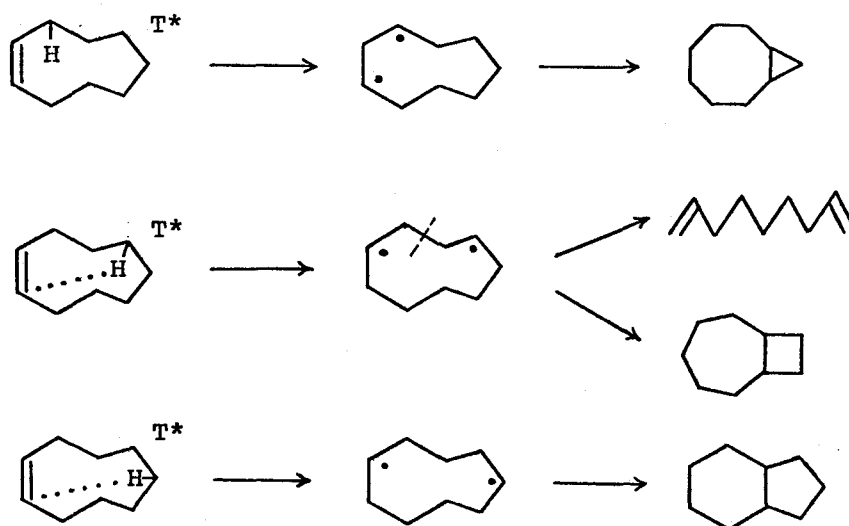
Scheme 4

It is thus confirmed in this system that the 1,2-shift of allylic hydrogen and the intramolecular hydrogen abstractions via six-membered transition states are the main course of the photosensitization of simple cyclic alkenes in the vapor phase.

References and Footnotes

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17) The recovered cycloheptene-d$_2$ was found not to undergo the deuterium scrambling.

18) A complex of 1c with excited mercury may be postulated as the precursor of the transannular hydrogen abstraction. It was reported that saturated hydrocarbons form mercury complexes which show new uv emissions in the region 250-280 nm. Unsaturated hydrocarbons, however, do not show new uv emission and are considered not to form such complexes (O. P. Strausz, J. M. Campbell, S. De Pauli, H. S. Sandhu, and H. E. Gunning, J. Amer. Chem. Soc., 95, 732 (1972)). The formation of 2 and 4 in benzene sensitization also suggests that a vibrationally excited triplet of 1c is more probable than a mercury complex as precursor.

19) Actually a biradical similar to 7 posturated in the mercury photosensitization of cyclohexene vapor[3] cyclizes to vinylcyclobutane. Any formation of cyclohexene and vinylcyclobutane could not be observed in the photosensitization of 1c.

20) a) C. D. Gutsche and J. W. Baum, J. Amer. Chem. Soc., 90, 5862(1968); b) E. J. Corey and E. Block, J. Org. Chem., 34, 1233(1969).

21) The deuterium distribution in the resulting hexadiene-d$_2$ could not be confirmed.

22) In this work, only half the hydrogens at the 5- and 6-positions of 1c were replaced by deuterium. The term 'k$_H$/k$_D$' means k$_2$ for 1c/k$_2$ for the labelled isomer.

23) See for example, P. J. Wagner, Accounts Chem. Res., 4, 168(1971).

24) A recent report of Hornback on the photolysis of 1,4-diphenylpent-4-en-1-ol presents another example of a hydrocarbon analogue of a Norrish type II photocleavage(J. Amer. Chem. Soc., 96, 6773(1974)).

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2-2   Triplet Sensitization of Acyclic Alkene Vapor

In the preceding section, it is shown that the vibrationally excited triplet of cyclooctene and cyclononene undergoes an efficient intramolecular γ-hydrogen abstraction through a cyclic, six-membered transition state, resulting in the formation of a cyclic 1,4-biradical. The 1,4-biradical thus formed undergoes competitive β-cleavage and cyclization, which provides an olefinic analogue with the Norrish type II reaction of carbonyl compounds.[1] Although the mechanism has not been fully clarified, the mercury sensitization of 1-pentene vapor also gives products which may be attributed to the intramolecular γ-hydrogen abstraction and the subsequent reaction of the resulting 1,4-biradical.[2,3] Consequently, it is suggested that the vibrationally excited π,π* triplet of alkenes containing a γ-hydrogen atom shows an analogous reactivity with the type II photocleavage of carbonyl compounds, although the mechanism of vapor-phase photosensitization of alkenes has hitherto mainly involved the allylic C-C and C-H bond fissions.

In this section the auther will discuss the detailed mechanism, generality, and importance of the intramolecular hydrogen abstraction reaction in the vapor-phase photosensitization of simple alkenes.

Experimental

Materials.——— 1-Hexene(**1**). Commercially available 1-hexene was purified by distillation through a spinning band column and preparative glc on PEG to a purity of >99.9%.

1-Hexene-5,5-d_2(**1d**). The deuterium labelled hexene was prepared in a three step process starting from hex-5-en-2-one. The procedure consisted in $LiAlD_4$ reduction of the hexenone to hex-5-en-2-ol-2-d, followed by esterification with p-toluenesulfonyl chloride to the tosylate and subsequent reduction with $LiAlD_4$ to give **1d**. The product was purified by preparative glc to a purity of >99.9%. The nmr spectrum of **1d** showed three vinyl protons at δ 5.7(t-q), 4.9(d), and 4.85(d), two allylic protons at 2.0(q), two methylene protons at 1.32(t), and three methyl protons at 0.88(s) in accord with the structure of **1d**. The isotopic purity of **1d** was determined to be 98.7% by nmr and mass spectrometry.

cis-2-Octene(**2c**). Commercially available cis-2-octene containing 5% trans-isomer was purified by preparative glc on PEG to a purity of 99.1%.

The experimental sample contained a small amount (0.87%) of the trans-isomer (2t) as an impurity. A correction was applied to all of the data for the presence of the impurity.

General procedure.———— All the experiments were carried out at 25±1°C and under static conditions. The apparatus employed in the mercury sensitization was the same as described in the preceding section. Control runs revealed that no detectable reaction occurred in the absence of uv irradiation. The quantum yields for the mercury sensitization of 1, 1d, and 2c were determined by propane actinometry at 300 torr, where $\phi(H_2)$ was taken as unity.[4] The absorption of the incident radiation was incomplete in the cell and appropriate corrections were made in the determination of the quantum yields.

After each run, products were trapped in a capillary at -196°C; small amounts of the non-condensable products were discarded. The condensables were analyzed by glc on a 6 m column of 20% squalane at 50°C for the products from 1-hexene, and on a 6 m column of 25% β,β'-oxydipropionitrile (ODPN) at 50°C for those from 2-octene. The gas chromatographic analysis of the saturated compounds produced in the mercury sensitization of 2c was conducted with a 15 cm column of $HgSO_4$-scrubber, Absorite PM (Tokyo Kasei Co.), which absorbs only olefinic and aromatic compounds selectively,[5] since some peaks of the saturated products were partially submerged in the peak of 2-octene. All products, which can be separated from each other under these conditions, had retention times on glc and mass spectra identical with those of commercially obtained or independently synthesized authentic specimens. No searching attempt on glc was made for dimeric products.

Independent synthesis of authentic specimens.———— The structures of the compounds synthesized were confirmed by means of nmr, ir, and mass spectrometry.

cis- and trans-1,2-Dimethylcyclobutanes (3c and 3t). The diethyl ester of trans-cyclobutane-1,2-dicarboxylic acid was converted to a mixture of cis- and trans-diesters by sodium-catalyzed epimerization in ethanol.[6] The mixture (cis/trans=0.15) of diesters was reduced to a mixture (cis/trans=0.12) of cis- and trans-1,2-dimethylcyclobutanes 3 in a three step process composed of $LiAlH_4$ reduction into cis- and trans-1,2-bis (hydroxymethyl) cyclobutanes, esterification with p-toluenesulfonyl chloride to the corresponding ditosylates, and in turn $LiAlH_4$ reduction of the ditosylates. Separation by preparative glc gave the pure specimens of 3c and 3t.

cis- and trans-1,2-Diethylcyclobutanes (6c and 6t). Photodimerization

of 1,3-butadiene[7] was performed in the presence of Michler's ketone as a sensitizer to give a mixture of cis- and trans-1,2-vinylcyclobutanes and 4-vinylcyclohexene(13, 83, and 4%, respectively). Hydrogenation of the mixture over 5% Pd-charcoal gave a mixture of cis- and trans-diethylcyclo-butanes 6 and ethylcyclohexane, from which the pure specimens of 6c and 6t were separated by glc.

cis- and trans-1-Methyl-2-ethylcyclopentanes(7c and 7t). cis-Bicyclo-[3.3.0]oct-2-ene, prepared by potassium-catalyzed cyclization of 1,3-cyclo-octadiene,[8] was converted to cis-1-hydroxymethyl-2-(2-hydroxyethyl)cyclo-pentane by ozonolysis at 0°C and subsequent reductive cleavage of the ozonide with NaBH$_4$ according to a similar procedure described by Sousa and Bluhm.[9] The cis-diol obtained was reduced to cis-1-methyl-2-ethylcyclopentane 7c by the same successive treatment employed in the synthesis of 3c and 3t. trans-Methylethylcyclopentane 7t was prepared by acetone-sensitized photoepimeri-zation[10] of 7c.

Results

Mercury-sensitized photolysis of 1-hexene(1).——— As major products, propene and cis- and trans-1,2-dimethylcyclobutane(3c and 3t) were obtained along with minor amounts of methylcyclopentane(4), cyclohexane(5), and n-hexane. The quantum yields of the products are shown in Table 1. Although trace amounts($\phi \leq 0.002$) of ethylene and 2-butenes were observed at substrate pres-sure$\leq$10 torr, any formation of these products was not detected in signific-ant yield at higher pressures; no detectable propane was produced at any pressure employed.

The product distribution for a short reaction time(1 min) exactly accorded with the results shown in Table 1, thus indicating that these are the primary photoproducts.

TABLE 1. Mercury photosensitization of 1-hexene (1) and 1-hexene-5,5-d_2 (1d)

Compound	Pressure (torr)	Irradiation time (min)	Product ϕ					
			Propene	3c	3t	4	5	n-Hexane
1	10	5	0.30	0.025	0.038	0.006	0.003	0.002
1 + NO^a	10	5	0.30	0.023	0.034	0.005	0.003	b
1d	10	5	0.158	0.013	0.020	0.006	0.003	c
ϕ_H/ϕ_D	—	—	1.91	1.87	1.87	1.0	1.0	—

^{a}Nitric oxide (1 torr) added.
^{b}Not detected.
^{c}Yield not determined.
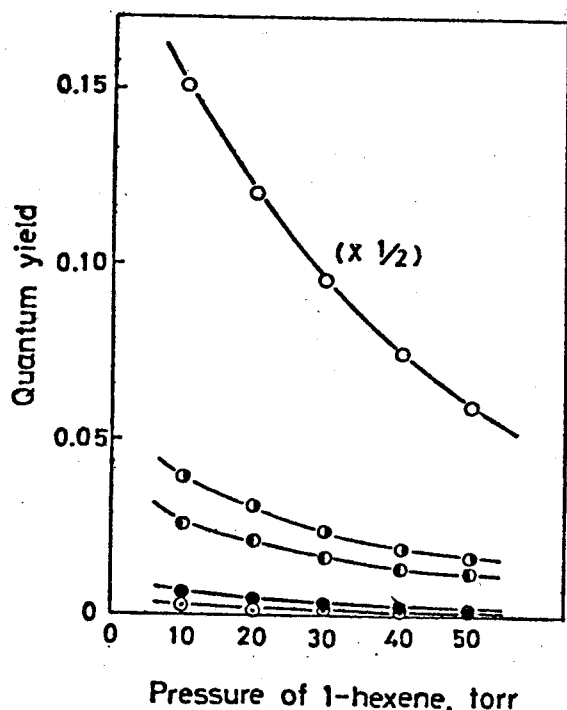
Fig. 1. Product yield as a function of 1-hexene pressure; irradiation time 5 min. O, propene (X½); ⊙, ⊘, cis- and trans-dimethylcyclobutane (3c and 3t); ●, methylcyclopentane (4); ⊘, cyclohexane (5).
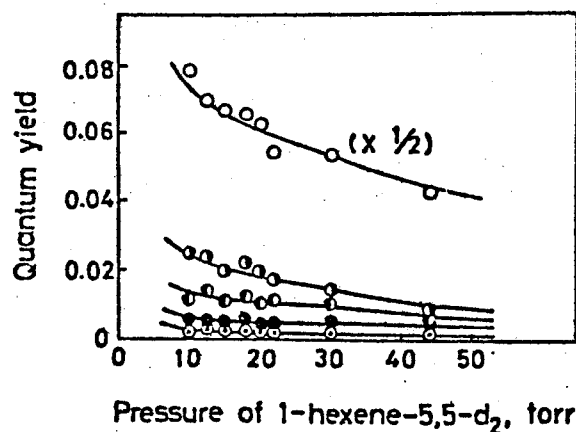
Pressure of 1-hexene, torr

Pressure of 1-hexene-5,5-d_2, torr

Fig. 2. Product yield as a function of 1-hexene-5,5-d_2 pressure; irradiation time 5 min. O, propene-d_1 (X½); ⊙, ⊘, cis- and trans-dimethylcyclobutane-d_2; ●, methylcyclopentane-d_2; ⊙, cyclohexane-d_2.

A scavenging experiment was performed with a small amount of added nitric oxide to suppress free radical-induced reactions which is familiar to mercury photosensitization of hydrocarbons.[11,12] As shown in Table 1, the formation of n-hexane was completely suppressed by the addition of nitric oxide, while the yields of the other major products were vertually invariant.

The effect of the initial substrate pressure on the product yields was examined up to 51 torr. The results are shown in Fig. 1. The suppressing effect of the increasing pressure on the yields of propene, dimethylcyclobutanes 3, methylcyclopentane 4, and cyclohexane 5 is evident from the data.

Since the formation of the cyclobutanes 3 was considered to involve hydrogen abstraction at the 5-position of 1-hexene, 5,5-dideuterated 1-hexene 1d was synthesized and subjected to mercury sensitization in other to examine isotope effects on the reaction. The photolysis of the deuterated hexene 1d was carried out under comparable conditions to afford similar results but showed a remarkable decrease in the yields of propene and the cyclobutanes 3, as shown in Table 1. Any detectable decreases in deuterium content were not observed by mass spectrometric analysis of the products 3-5. Mass spectrometric analysis also revealed that more than 88% of the propene produced contains one deuterium atom, suggesting predominant transfer of a deuteium atom at the 5-position of 1d.

The pressure-dependence study was repeated for the mercury sensitization of the deuterated hexene under comparable conditions, since the deuteration at the 5-position of 1 is expected to affect the rate of hydrogen abstraction, as well the quantum yields of propene and the cyclobutanes. As can be seen from Fig. 2, the product yields decreased with increasing pressure as in the case of 1 except for the greater reduction of the yields of propene and the cyclobutanes.

In the other experiments, it was observed qualitatively that the vapor-phase photosensitization[13] of 1 (10 torr) at 254 nm with benzene vapor (10 torr) as a sensitizer also gave the same major products, i.e. propene and the dimethylcyclobutanes 3 in a molar ratio of ca. 20:1 while 65 hr irradiation of benzene solution of 1 in a quartz tube by a 500 W high pressure mercury lamp produced no detectable yields of propene, 3, 4, and 5.

Mercury-sensitized photolysis of cis-2-octene (2c). ——— The major photolysis product was trans-2-octene (2t), and additionally minor amounts of 1-butene, cis- and trans-1,2-diethylcyclobutanes (6c and 6t), cis- and trans-1-methyl-2-ethylcyclopentanes (7c and 7t), and cis- and trans-1,2-dimethylcyclohexanes (8c and 8t) were obtained. Although 1-octene was also produced (ϕ=ca. 0.01 at 10 torr), accurate determination of its yield is difficult because of the incomplete separation on glc. The quantum yields are shown in Table 2. Any formation of n-butane and 2-butenes was not detected in significant amount. A short irradiation time (1 min) experiment gave the same product distribution as shown in Table 2, indicating that these are the primary products.

The effect of added nitric oxide was examined and the results are shown in Table 2. The addition of the radical scavenger inhibited completely the formation of n-octane, while the yields of the other products were not practically affected.

The pressure-dependence study on the mercury sensitization of 2c was performed up to 350 torr by adding xenon as an inert gas, since the range available was limited by the low vapor pressure of the substrate at room

TABLE 2. Mercury photosensitization of cis-2-octene (2c)

Pressure (torr)		Irradi-ation time (min)	Product ϕ							
2c	NO		1-Butene	6t	6c+8t[a]	7t	7c	8c	2t	n-Octane
10	0	5	0.084	0.008	0.010	0.002	0.003	0.003	0.44	0.005
10	1.0	5	0.088	0.008	0.010	0.002	0.002	0.003	0.44	b

[a] The combined yield of 6c and 8t is shown because of incomplete separation on glc.
[b] Not detected.

temperature. The results are plotted in Fig. 3. In order to avoid complicated plots on the figure, the results for the yields of 6c, 7c, 7t, and 8t are omitted because of their similar pressure dependences. The yield of n-octane stayed constant over the entire pressure range employed, in accord with the nature of the well-known radical-induced reactions. The product yields except that of 2t decreased gradually with increasing xenon pressure; the quantum yield of 2t contrarily increased to 0.49 and then remained constant at pressures ≥ 50 torr.
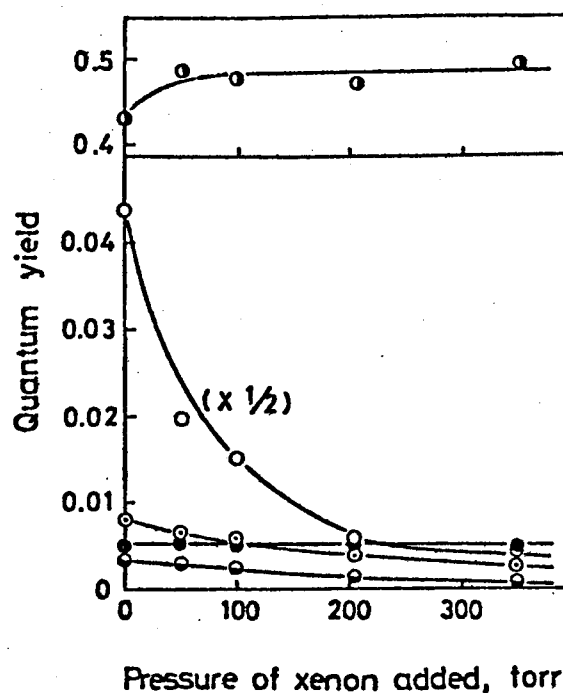
Fig. 3. Product yield as a function of xenon pressure in the mercury photosensitization of cis-2-octene (10 torr); irradiation time 5 min. ◑, trans-2-octene (2t); ○, 1-butene (X⅓); ⊙, trans-1,2-diethylcyclobutane (6t); ◒, cis-1,2-dimethylcyclohexane (8c); ●, n-octane.

Discussion

The pressure dependence of the product yields and the lack of inhibition by nitric oxide indicate the intermediacy of the vibrationally excited triplet state of the alkenes 1-hexene and cis-2-octene, consistent with the accepted view of the mercury photosensitization of alkenes. The formation of the
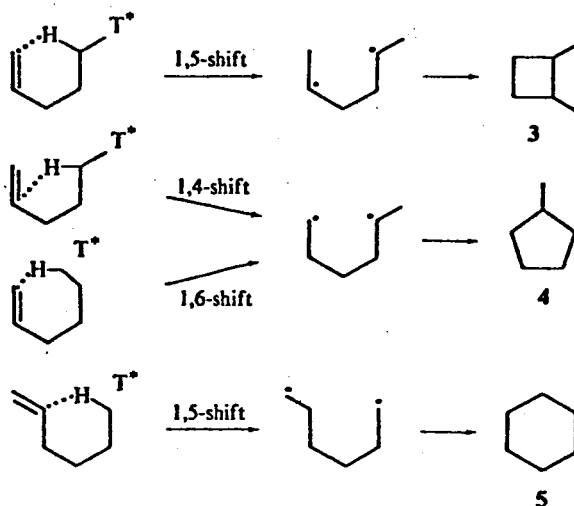
Scheme 1

cyclic compounds 3-5 in the photolysis of 1-hexene can be interpreted in terms of four intramolecular hydrogen abstraction processes followed by closure of the resulting biradicals(Scheme 1).

The mechanism which involves the familiar allylic C-C bond fission is ruled out for the formation of propene, since propane and 1,5-hexadiene which, if the allylic fission is operative, should be produced by the reaction of propyl and allyl radicals were not detected.[14] The negligible effect of the radical scavenger NO on the yield of propene also suggests the absence of any radical species as an intermediate. The formation of propene is interpreted in terms of competitive β-cleavage of the 1,4-biradical generated by the 1,5-hydrogen shift through a six-membered transition state as shown in Scheme 2.
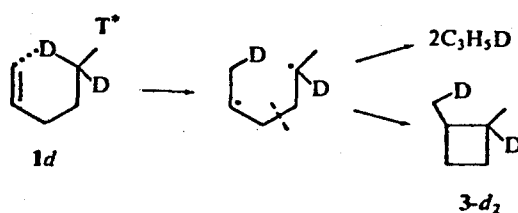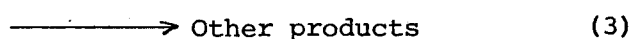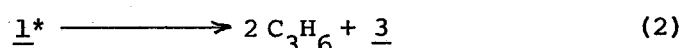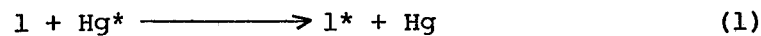

SCHEME 2

The above mechanism for propene formation is supported by the results of deuteration experiment that 1) >88% of the propene produced in the mercury sensitization of 1d contained one deuterium, and 2) both yields of propene and the dimethylcyclobutanes 3 decreased to a similar extent upon deuteration at the 5-position of 1-hexene(see ϕ_H/ϕ_D in Table 1).

Intramolecular hydrogen abstraction in the six-membered transition state, followed by competitive cyclization and β-cleavage of the resulting 1,4-biradical, may correspond to the Norrish type II reaction of carbonyl compounds.[1] Other cyclic products also involve intramolecular hydrogen abstractions(Scheme 1); methylcyclopentane 4 is formed from a 1,4- and/or 1,6-shift via unfavorable five- and/or seven-membered transition states, and, because of the unfavorable primary 1,6-biradical intermediate, a small amount of cyclohexane 5 is formed. Although this olefinic analogue of the Norrish type II reaction does occur upon benzene sensitization of 1 in the vapor phase, no detectable product from these intramolecular hydrogen abstraction reactions was observed in the liquid-phase benzene sensitization of 1. Therefore, the olefinic type II reaction, and the other intra-

molecular hydrogen abstractions as well, are characteristic of the vibra-tionally excited triplet generated in the vapor-phase photosensitization.

The pressure dependence study of the photolysis of $\underline{1}$ and $\underline{1d}$ gives additional information on the lifetime of the excited triplet and the iso-tope effect on the rate of hydrogen transfer. The sequence 1-5 is proposed for the formation of propene and cyclobutanes $\underline{3}$,

$$\underline{1} + Hg^* \longrightarrow \underline{1}^* + Hg \tag{1}$$

$$\underline{1}^* \longrightarrow 2\,C_3H_6 + \underline{3} \tag{2}$$

$$\longrightarrow \text{Other products} \tag{3}$$

$$\longrightarrow \underline{1} \tag{4}$$

$$\underline{1} \longrightarrow \underline{1} \tag{5}$$

where the asterisk represents the excited triplet state.

A steady-state treatment of the sequence 1-5 leads to the equation 6 for the reciprocal of the quantum yield of the type II reaction, i.e. the com-bined yield of propene $X\dfrac{1}{2}$ and $\underline{3}$.

$$1/\phi_{\text{type II}} = \frac{k_2 + k_3 + k_4}{k_2} + \frac{k_5}{k_2}[\underline{1}] \tag{6}$$

In Fig. 4, the reciprocal of the combined yield of propene $X\dfrac{1}{2}$ and $\underline{3}$ from the photolysis of $\underline{1}$ and $\underline{1d}$ are plotted against the substrate pressure and good linear relations are obtained.

From the slopes and the inter-cepts, following ratio was obtained: $(k_2 + k_3 + k_4)/k_5 = 17.7$ and 24.5 torr in the photolysis of 1-hexene and 1-hex-ene-d_2, respectively. Assuming that the deactivation of triplet hexene occurs at each collision, i.e. $k_5 =$
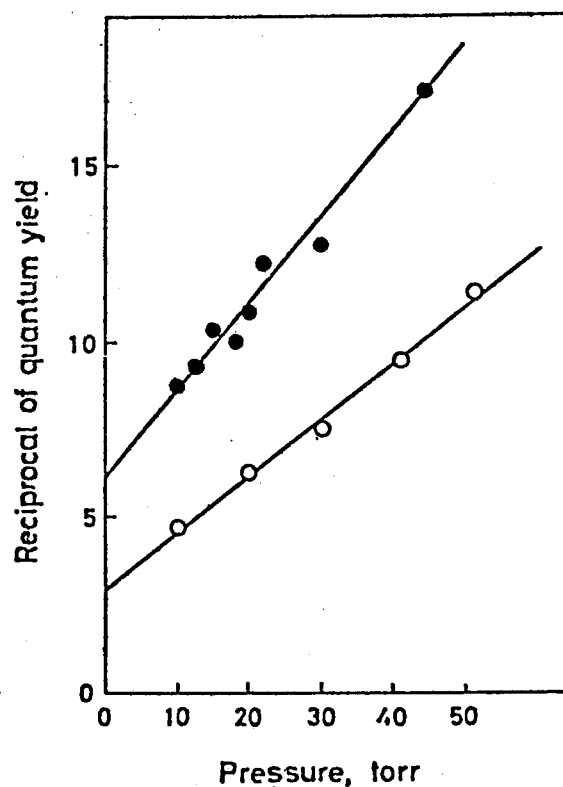

FIG. 4. Reciprocal of quantum yield of the olefinic type II reaction as a function of the substrate pressure in the mercury photosensitization of 1-hexene (O) and 1-hexene-5,5-d_2 (●).

1.0×10^{-10} cc/molecule·sec,[15,16] $k_2 + k_3 + k_4$ equals 0.56×10^8 sec^{-1}. Thus the 1-hexene triplet has a lifetime of 1.8×10^{-8} sec. A similar calculation gives the lifetime of the deuterated 1-hexene triplet, 1.3×10^{-8} sec.[17] These values are in fair agreement with the results of other alkene triplets, e.g. 6.3×10^{-9} sec for 1-butene[15] and 5.0×10^{-9} sec for cyclohexene.[16] On the assumption that the cross sections of $\underline{1}$ and $\underline{1d}$ do not differ too greatly, the isotope effect on the rate of process 2, denoted by k_H/k_D, is estimated from the slope of equation 6. From Fig. 4, the value k_H/k_D for the olefinic type II reaction is calculated to be 1.5, and the isotope effect on the zero pressure extrapolated quantum yield, designated by $(\phi_H/\phi_D)_o$, is also calculated to be 2.1 from the intercepts. These are consistent with the mechanism involving the intramolecular 1,5-hydrogen transfer process.

With the mercury photosensitization of cis-2-octene, where cis-trans isomerization can be observed, 1-butene and the cis- and trans-isomers of three cyclic products $\underline{6-8}$ were obtained along with trans-2-octene $\underline{2t}$. Based on the observed suppressing effect of added xenon on the product yields and the lack of inhibition by nitric oxide, the formation of 1-butene and the other cyclic products should be interpreted in terms of the intramolecular hydrogen abstractions of the hot triplet 2^* as shown in Scheme 3. Deactivation of the hot triplet by collision leads to the cis-trans isomerization as the major photoreaction.

SCHEME 3
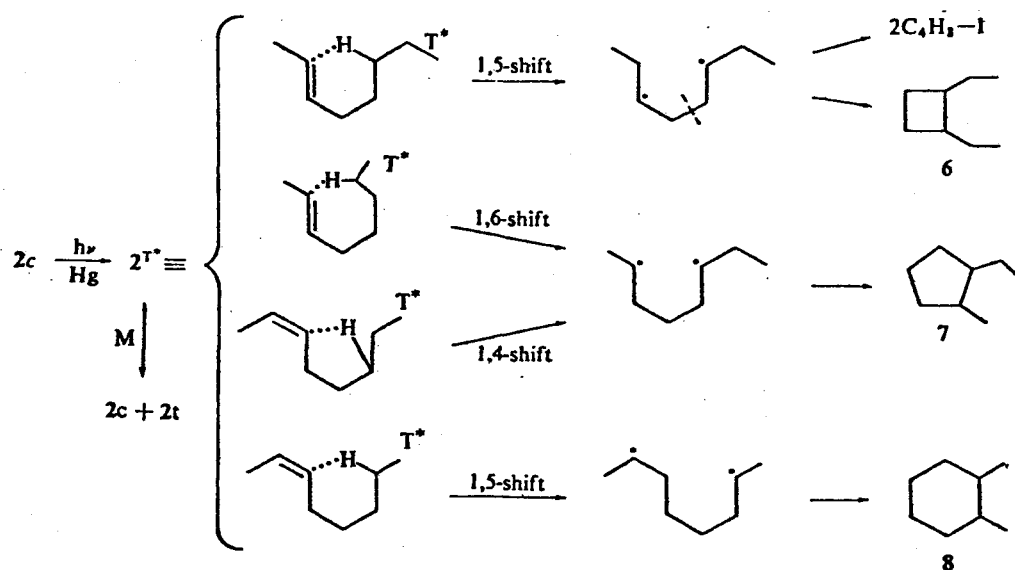
The lower yield for the intramolecular hydrogen abstraction reactions in the photosensitization of 2-octene may be attributable to the greater freedom in vibration and rotation than that of 1-hexene, since intramolecular relaxation of excess vibrational energy is considered to diminish the rate of the hydrogen abstractions.

TABLE 3. Mercury photosensitization of some alkenes[a]

Alkene	Press (Torr)	Allylic C—C fission	Olefinic type II reaction	Cyclopropane formation	cis–trans Isomerization	Other reactions	Reference
1-Butene	14.7	0.48[c]	—	0.04	—	<0.01	15
2-Butene	30	e	—	e	0.50	<0.01	18
1-Pentene[b]	15	5%	72%	f	—	22%	2
1-Hexene	10	e	0.21	e	—	0.02	This work
cis-2-Octene	10	e	0.06	e·	0.44	0.01	This work
Cyclopentene	30	0.24	—	e	—	0.03[d]	19
1-Methylcyclopentene	10	0.20	—	e	—	0.01	20
Cyclohexene	10	0.20[c]	—	0.01[h]	—	0.01	16, h
3-Methylcyclohexene	10	0.02	—	e	—	0.02	21
cis-4,5-Dimethylcyclohexene	9	0.008	—	e	—	0.03	This work
trans-4,5-Dimethylcyclohexene	9	0.008	—	e	—	0.03	This work
Cycloheptene	6	>0.05	>0.04[h]	0.09	—	<0.03	This work
cis-Cyclooctene	4.5	e	0.34	0.05	0.08	0.03	This work
cis-Cyclononene[b]	1.0	e	43%	57%	f	e	This work

[a]Shown in quantum yield reported, unless otherwise noted.
[b]Shown in % composition, since yields have been reported in μmol.
[c]Combined yield of allylic C—C and C—H bond fission.
[d]Dimeric products (ϕ =0.43) were also obtained.
[e]Formation not reported.
[f]Yield not determined.
[g]References 26 and 27.
[h]Unpublished results of the author.

The results of the mercury photosensitization studies of simple alkenes so far reported are summarized in Table 3. Reactions of the vibrationally excited triplet of alkenes may be classified according to the primary processes; 1) the allylic C-C and C-H bond fission, 2) the intramolecular hydrogen abstraction, mainly the olefinic type II reaction, 3) the 1,2-shift of allylic hydrogen providing cyclopropanes, and 4) the cis-trans isomerization as the result of collisional deactivation of the triplet. Other miscellaneous reactions reported are also listed. As shown in Table 3, the major photoreaction of the vibrationally excited triplet of open-chain alkenes without a γ-hydrogen is merely the allylic C-C and C-H bond cleavages in addition to the cis-trans isomerization. The alkenes carrying a γ-hydrogen atom contrarily undergo the olefinic type II reaction upon mercury photosensitization instead of the allylic fission. Regarding cycloalkenes, steric restrictions in cyclopentene and cyclohexene completely prevent intramolecular hydrogen abstraction and allylic fission is predominant, while

the larger cyclic alkenes do undergo the type II reaction in high yield, especially in the photolysis of cyclooctene.

It is thus concluded that the vibrationally excited π,π^* triplet of simple alkenes with a γ-hydrogen mainly undergoes intramolecular hydrogen abstraction in a six-membered transition state, although the main course of the reaction of the triplet alkenes with vibrational activation had previously been believed to be the well-known allylic bond cleavage.

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Chapter 3   Comparison of Direct and Sensitized Photolysis of
             Simple Alkenes: Effects of Spin Multiplicity and
             Vibrational Activation

3-1   Vapor-phase Photolysis of cis- and trans-4,5-Dimethyl-
       cyclohexenes

Few studies have been reported on the direct photolysis of cycloalkenes,
although there is some literature on the mercury-sensitized photolysis of
these species.[1]   Regarding the cyclohexene derivatives dealt with in this
section, Gunning et al. have investigated in detail the kinetics of the
mercury-sensitized photolysis of cyclohexene itself.[1a]
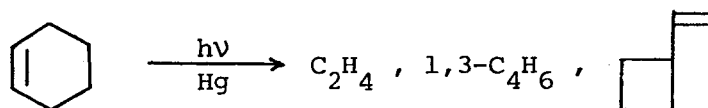
They proposed a biradical mechanism for the formation of ethylene, butadiene
and vinylcyclobutane, which involves an alkyl-allyl biradical produced by
the familiar allylic C-C bond cleavage, and the kinetics seem to support
this mechanism.   De Maré has reported on the mercury-sensitized photolysis
of 3-methylcyclohexene vapor via similar reaction mechanism.[2]   However,
little evidence has been obtained regarding the nature of the intermediate
species and the mechanism involved.

Recently it has been shown that the spin multiplicity of the inter-
mediate 1,4-biradical drastically affects the stereochemistry of the reaction
in Norrish type II photocleavage,[3] as well as in other systems.[4]   A study
of the direct and sensitized photolyses of cis- and trans-4,5-dimethylcyclo-
hexenes(lc and lt) is of interest since the results are expected to provide
insight into both the reaction mechanism and the spin correlation effects.

Experimental

Materials.———— cis- and trans-4,5-Dimethylcyclohexenes were prepared accord-
ing to the procedure similar to those described by Peter et al.[5]   cis-4,5-
Bis(hydroxymethyl)cyclohexene, prepared by the reduction of cis-cyclohexene-

4,5-dicarboxylic anhydride with LiAlH$_4$ in ether, was converted into ditosyl-
ate by a reaction with p-toluenesulfonyl chloride in dry pyridine. The cis-
ditosylate was reduced in turn to cis-4,5-dimethylcyclohexene 1c. The di-
methyl ester of trans-cyclohexene-4,5-dicarboxylic acid, prepared by a Diels-
Alder reaction of dimethyl fumarate with 1,3-butadiene at 200°C for 3 hr in
an autoclave,[6] was reduced to trans-4,5-dimethylcyclohexene 1t by similar
successive treatments with LiAlH$_4$, p-toluenesulfonyl chloride, and again
LiAlH$_4$. All the compounds prepared were identified by means of ir and
nmr spectrometry. cis- and trans-Dimethylcyclohexenes thus obtained were
purified by preparative glc on PEG column. Quantitative analysis by glc
indicated that the purities of 1c and 1t are at least 99.9 and 98.0%, re-
spectively. Samples of 1t contained a small amount (1%) of 1c as an impurity.
A correction was applied to all the data for the presence of the impurity.
The samples of 1c and 1t were admitted to a vacuum line, dried over evapo-
rated sodium, and degassed at liquid nitrogen temperature before use.

The nmr spectra of 1c and 1t were in good agreement with those reported
by Peter et al.[5] Their steric configurations were confirmed by the glc
comparison of commercially available cis- and trans-dimethylcyclohexanes
with the saturated compounds obtained by the hydrogenation of 1c and 1t on
5% Pd-charcoal.

Apparatus and procedure.——— All the experiments were carried out at room
temperature and under static conditions. The apparatus employed in the
mercury photosensitization and direct photolysis at 185 nm was the same as
described in the preceding Chapters. The quantum yields in the mercury
sensitization were determined by ethylene (100 torr) actinometry.[7]

The condensable products at -196°C were analyzed by glc on a 6 m column
of 20% ODPN at 50-70°C. The stereoisomers of 2-butene were clearly sepa-
rated from one another under these conditions, while a trace amount of the
stereoisomers of 1 could not be separated from one another enough for quan-
titative analysis, especially in the higher pressure (> 3 torr) experiments.
The analyses of the dimeric products from the mercury sensitization were
conducted by glc on a 3 m column of polyethylene glycol-6000 at 150°C and
1.5 m column of FFAP at 150°C. The molecular weights of the dimers were
confirmed using a Hitachi RMS-4 gc-mass spectrometer.

Identification of 2,3-Dimethyl-vinylcyclobutane (3).——— Mercury sensitiza-
tion of 1c was carried out in a preparative scale using the mercury lamp
and the preparative irradiation apparatus of 5 1 volume. The irradiation
of 1c with 10% nitric oxide in the presence of mercury was run at 1 torr

for 15 hr. The photolyzed sample was trapped at liquid nitrogen tempera-
ture and then subjected to preparative glc in order to isolate 3. The nmr
spectrum of 3 was obtained with TMS as an internal standard in CCl_4 and
showed three vinyl protons at δ 5.5-6.0(m), 4.9(d), and 4.95(d), six methyl
protons at 1.0(d), and five cyclobutyl protons at 1.2-2.2(m). The mass
spectrum indicated the following relative intensities: m/e, 110(2.1), 95
(28.3), 81(40.5), 69(45.5), 68(67.8),67(70.7), 56(35.1), 55(100), and 54
(6.4). These spectral data indicate a 2.3-dimethylvinylcyclobutane struc-
ture of 3, but its steric configuration is not known. The mercury sensi-
tization of 1t also produced a compound which has the same retention time
on glc and identical mass spectrum with that of 3. Consequently, it is
considered that the mercury photosensitization of both 1c and 1t produced
dimethylvinylcyclobutane 3 with an identical steric configuration.

Identification of 3,4-dimethyl-1-methylenecyclopentane(2).—— Eighty mg
of 1c in a sealed Suprasil tube, 2 mm in diameter, was photolyzed in the
liquid phase without a solvent using a 30 W low-pressure mercury lamp.
The irradiation was continued for 350 hr resulting in a conversion of ca.
10% and the photolyzed sample was subjected to preparative glc to isolate
2c. The nmr spectrum of 2c was obtained with TMS in CCl_4 and showed two
olefinic protons at δ 3.5(s), six methyl protons at 0.86(d), and six other
protons at 1.8-2.4(m). The mass spectrum of 2c indicated the following
relative intensities: m/e, 110(26.9), 95(100), 81(32.6), 69(20.0), 68(32.3),
67(60.0), 55(47.7), and 54(26.2). The glc analysis on an ODPN column indi-
cated that the isolated C_8H_{14} isomer has a shorter retention time relative
to those of the authentic samples of cis-3,4-, trans-4,5-, cis-4,5-, 2,3-,
1,2-dimethylcyclohexenes and 2-methyl-1-methylenecyclohexane, and that the
retention time of the saturated compound, prepared by hydrogenation of 2c
on Pd-charcoal, is different from that of trans- or cis-1,2-dimethylcyclo-
hexane. All the data described above suggest a 3,4-dimethyl-1-methylene-
cyclopentane structure for 2c, the steric configuration of which is deduced
to be cis from that of the starting material(1c).

Vapor-phase direct photolysis of 1c produced the same C_8H_{14} compound(2c),
the mass spectrometric, glc, and chemical(hydrogenation) features of which
were identical with those of the 2c obtained in the liquid-phase photolysis
of 1c. Vapor-phase photolysis of 1t afforded another C_8H_{14} isomer(2t),
which has a shorter retention time on ODPN relative to 2c. The mass spectrum
of 2t indicated: m/e, 110(33.0), 95(100), 81(41.7), 69(33.0), 68(46.1), 67
(60.0), and 55(54.8). The structure of 2t was identified to be trans-3,4-

dimethyl-1-methylenecyclopentane on the basis of resemblance of the mass spectrum.

Results

Direct photolysis.——— As major decomposition products, 2-butene and 1,3-butadiene were obtained together with a minor isomeric product, 3,4-dimethyl-1-methylenecyclopentane(2), in the direct photolysis of 1c and 1t at a substrate pressure of 5 torr, as shown in Table 1. Dimeric products and a vinylcycloalkane derivative, which are usually produced in the mercury-sensitized photolysis of cycloalkenes,[1] were not detected in significant yields. The combined yield of 2-butene was equal to that of butadiene. The photolysis of 1c and 1t at 5 torr gave almost specifically cis- and trans-2-butenes at cis-trans ratios of 16:1 and 1:20, respectively. Irradiation of 1 through a UV-25 filter did not result in any products under comparable conditions.

The effects of exposure time on the product yields were examined in the photolysis of 1c at a pressure of 8 torr, since the further irradiation of initially formed 2-butene could produce isomeric 2-butene.[8] According to the data appearing in Fig. 1, all the yields increase linearly with exposure time, which indicates that these are the product from the primary process. The percentage of cis-2-butene, on the other hand, was constant over the range of 1-6 min, and therefore the isomeric 2-butene produced non-stereo-specifically cannot result from the further photoisomerization. Direct photolysis of 1c was performed over the pressure range of 1-8 torr. The results are shown in Fig. 2. Although the pressure range available was limited by the low vapor pressure of the substrate, the suppressing effect on the formation of butene and butadiene is evident from the data. The percentage of cis-2-butene was independent of the pressure, in spite of the decrease in the yields with increasing pressure. The yield of 2c remained constant over the entire pressure range.

TABLE 1. PRODUCTS OF DIRECT PHOTOLYSIS OF 1

Compd	Press, Torr	Exposure time, min	Products, μmol $\times 10^3$				
1c	5.0	1.0	53.8	3.4	61.7	5.1	a)
1t	5.0	1.0	2.8	57.0	61.7	a)	6.1

a) Not detected.
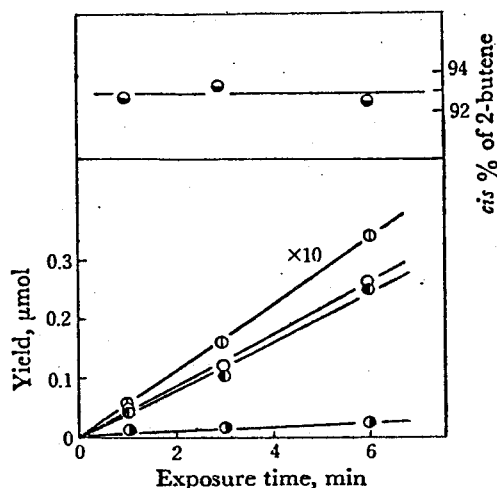
Fig. 1. Product yields as a function of exposure time in direct photolysis of 1c (8 Torr). ●, cis-2-butene; ◐, trans-2-butene; ○, 1,3-butadiene; ⊕, cis-3,4-dimethyl-1-methylenecyclopentane (×10); ◒, cis % of 2-butene.

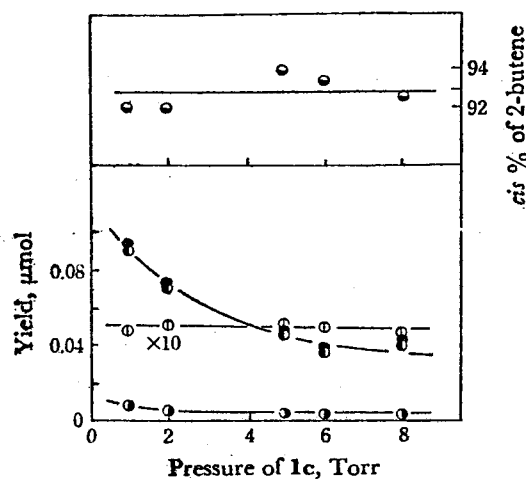Fig. 2. Product yields as a function of initial substrate pressure in direct photolysis of 1c. Exposure time is 1 min. ●, cis-2-butene; ◐, trans-2-butene; ●, 1,3-butadiene; ⊕, cis-3,4-dimethyl-1-methylenecyclopentane (×10); ◒, cis % of 2-butene.

Mercury-sensitized photolysis.—— The products of the mercury sensitization of **1** were hydrogen, 2-butene, 1,3-butadiene, 2,3-dimethylvinylcyclobutane (**3**), 1,2-dimethylcyclohexanes, and some dimeric products. The gas chromatographic and mass spectrometric analyses of the dimeric products showed that the dimeric fraction is composed of at least five compounds, the molecular weights of which are in the range of 218–222. The mass spectra of the dimers appears to suggest the absence of the cyclodimers of **1**. On the basis of these results and observations in other systems,[1] the dimeric products are assumed to have a bicyclohexyl, cyclohexylcyclohexene, or bicyclohexenyl skeleton. The quantum yields of all products except the dimers are shown in Table 2. The distribution of the products from shorter exposure time (1 min) experiments is in good agreement with this result. The combined yield of the 2-butenes equals that of butadiene. The 2-butene resulting from the mercury sensitization was predominantly trans even when

TABLE 2. PRODUCTS OF MERCURY-SENSITIZED PHOTOLYSIS OF 1

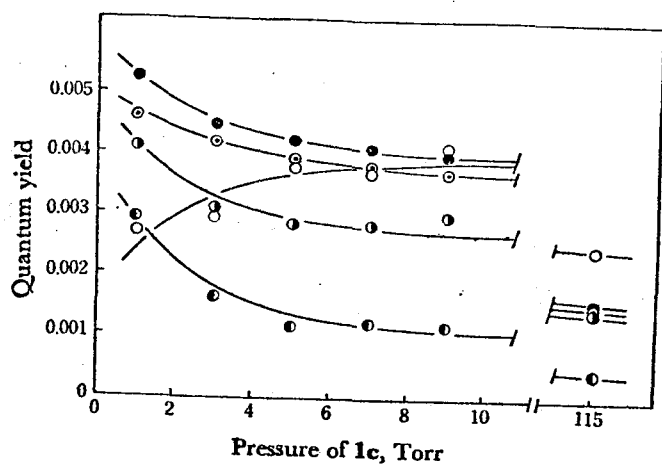| Compd	Press, Torr	Exposure time, min	Products, Φ × 10³						H₂
1c	9.0	3.0	1.2	3.0	4.0	3.7	3.7	a)	27.2
1t	9.0	3.0	0.6	3.0	3.7	3.0	a)	4.8	b)

a) Not detected.   b) Not determined.

Fig. 3. Product yields as a function of pressure in mer-cury-sensitized photolysis of 1c. Exposure time is 3 min. Plots at a pressure of 115 Torr were obtained by adding xenon (112 Torr) to 1c (3 Torr). ●, *cis*-2-butene; ◐, *trans*-2-butene; ●, 1,3-butadiene; ◉, 2,3-dimethyl-1-vinylcyclobutane; ○, *cis*-1,2-dimethyl cyclohexane.
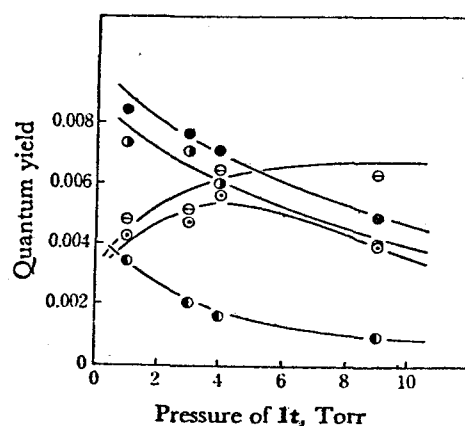
Fig. 4. Product yields as a function of substrate pressure in mercury-sensitized photolysis of 1t. Exposure time is 3 min. ●, *cis*-2-butene; ◐, *trans*-2-butene; ●, 1,3-butadiene; ◉, 2,3-dimethyl-1-vinylcyclobutane; ⊖, *trans*-1,2-dimethylcyclohexane.

1c was used.   In addition, the photolysis of both 1c and 1t produced di-methylvinylcyclobutane 3 having the same steric configuration as the major product.

A pressure-dependence study was also carried out for the mercury sen-sitization of 1c and 1t.   In order to further examine the pressure effects, a higher pressure experiment was performed above the vapor pressure limit of the substrate using 1c(3 torr) with xenon added(112 torr).   The results are plotted in Figs. 3 and 4.   While the suppressing effect of the pressure on the yields of 2-butene, butadiene, and 3 is evident, the 1,2-dimethyl-cyclohexane yields show no pressure dependence above ca. 5 torr in the photolysis of both 1c and 1t.

An inhibiting experiment was performed with a small amount of nitric oxide added since radical-induced reactions caused by excited mercury atom are well-known in the mercury sensitization of hydrocarbons.[9]   As can be seen from Table 3, the formation of 1,2-dimethylcyclohexane and the dimeric

TABLE 3.   EFFECTS OF NITRIC OXIDE ON MERCURY-SENSITIZED PHOTOLYSIS OF 1

Press, Torr		Exposure time, min	Products, μmol × 10³					
1c	NO		⌈	⌠	⌈	⊐⊨	⬡⟨	Dimers
5.0	0	3.0	4.0	9.7	14.4	13.4	12.9	138
5.0	0.5	3.0	5.5	7.5	9.0	10.0	a)	a)

a) Not detected.

products was completely suppressed by the addition of nitric oxide which acts as a radical scavenger, while the yields of the other products merely decreased to a small extent.

In other experiments, it was observed qualitatively that 1) the sensitized decomposition of 1c (5 torr) at 254 nm with benzene vapor (5 torr) as a sensitizer did not produce detectable amounts of any products and 2) irradiation at 185 nm of 1c in the liquid phase without a solvent produced no detectable yields of 2-butene, butadiene, or 3. The only detectable products were saturated cis-1,2-dimethylcyclohexane and isomerized cis-3,4-dimethyl-1-methylene-cyclopentane (2c).

Over the temperature range of 400-700°C, pyrolyses of 1c and 1t were conducted using a Shimadzu PYR-2A pyrolyzer-glc. The products of the pyrolysis were merely decompostion products of lower molecular weight, and no 2-butene, butadiene, or isomeric product was detected in significant yield.

Discussion

Decomposition of the retro-Diels-Alder type appears to be the main course of the direct photolysis of 1 in the vapor phase, which results in the stereospecific formation of 2-butene together with an equimolar amount of butadiene. No detectable amounts of 2-butene and butadiene were formed in the direct photolysis of 1 in the liquid phase. Irradiation through a UV-25 filter produced no products in the direct photolysis of 1 in the vapor phase. From these results and the stereospecificity of the reaction, it is inferred that 1 is promoted to an electronically excited singlet state by the 185 nm resonance line of mercury and then decomposes directly or via a short-lived biradical produced by an allylic C-C bond cleavage into 2-butene and butadiene with the retention of its original configuration. It is, however, difficult to determine if these are direct products from the electronically excited states or if significant amounts are formed as a result of decomposition after internal conversion to a vibrationally-excited ground state.

The most significant observation in the direct photolysis of 1c is the effect of pressure, resulting in a decrease in the yields of the decomposition products with increasing pressure, whereas the yield of cis-3,4-dimethyl-1-methylenecyclopentane (2c) remains constant. The 2c observed is, therefore, considered to be formed in a pressure-independent process,

probably from π,R(3s) Rydberg excited state(see Chapter 1). On the other hand, the high pressure dependence of the yields of the other decomposition products suggests that these are the products from a vibrationally-excited ground state, since with molecules of this size, the lifetimes should be long enough to permit collisional deactivation of any energetic ground-state species which may be formed via an internal conversion process. This elucidation is also supported by the observation that only 2c is formed in the liquid-phase photolysis of 1c, in which vibrational energy is quickly removed. Although 2-butene and butadiene were not detected in the attempted pyrolysis of 1 at 400-700°C, the vibrationally-excited ground state species as the intermediate in the direct photolysis cannot be eliminated from this result since raising the temperature from room temperature to 700°C is considered to involve very little energy difference relative to the large energy input of the direct photolysis.
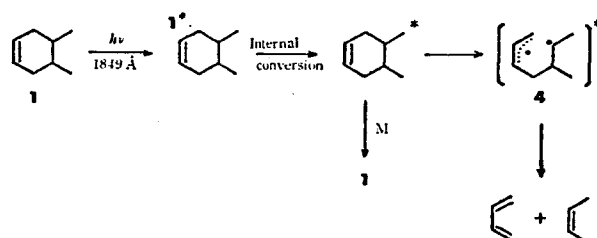
Scheme 1.

The detailed mechanism of the photodecomposition of 1 to 2-butene and butadiene is of interest in this section. The fact that several % trans-2-butene is formed from 1c and also cis-2-butene from 1t seems to suggest the biradical mechanism as opposed to the concerted path. However, there may be another possibility that the electronically-excited singlet state of 1 undergoes intersystem crossing in part to a triplet species, which would give nonstereospecific 2-butene in a manner similar to the sensitized photolysis described below. Although such a process is important in the photolysis of aromatic and carbonyl compounds,[10] it is believed that the large difference in energy causes singlet-triplet intersystem crossing to be very slow in such a monoolefin. The absence of the vinylcyclobutane 3 in the direct photolysis of 1 also indicates the low efficiency of the intersystem crossing since photoisomerization to 3 is characteristic of triplet species

as shown in the mercury sensitization of 1. It is therefore concluded that the photodecomposition of 1 proceeds via the short-lived singlet biradical 4; see Scheme 1.

In mercury photosensitization, 2,3-dimethyl-1-vinylcyclobutane 3, the cis-trans isomers of 1, and the radical-induced products, as shown in Table 2. Since the formation of 1,2-dimethylcyclohexane and the dimeric products was completely suppressed by the redical scavenger NO, these products, and probably hydrogen, are considered to be formed from the well-known hydrogen abstraction reaction initiated by the excited mercury atom.[1a,9]

In contrast to the direct photolysis, the 2-butene resulting from the mercury sensitization of 1 is predominantly trans regardless of the original configurations. Furthermore, the mercury sensitizations of 1c and 1t produced 2,3-dimethylvinylcyclobutane having the same steric configuration as a major product, and in addition the isomerization of 1c to 1t was confirmed at low pressure. On the basis of these results and the generally accepted view of mercury photosensitization of alkenes,[1,9,11] it is suggested that the vibrationally-excited triplet state of 1, produced by energy transfer from the excited mercury atom, undergoes the usual allylic C-C bond fission resulting in an allylic triplet biradical 4, where rotation about the C-C bond adjacent to the alkyl radical site is possible. Then the biradical [3]4 decomposes into cis- and trans-2-butenes with an equimolar amount of butadiene, and/or cyclizes to 1 or 3(see Scheme 2).
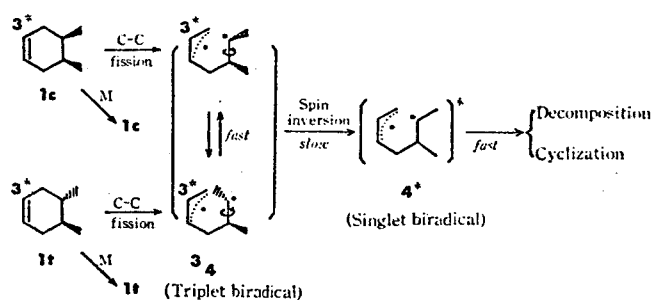
Scheme 2

Spin inversion is required in order for the triplet biradical [3]4 to undergo decomposition and/or ring closure. Although the present intermediate is an alkyl-allyl biradical, ring closure of the photolytically derived singlet 1,4-biradical has been shown to be fast relative to the time required for free rotation about the C-C bonds.[12] If the same is true in this system, equilibrium will be established among triplet, not

singlet, biradical rotamers.   The rate-determining step in the sensitized photolysis may, therefore, be the spin inversion of the triplet biradical.

· As for the benzene sensitization in the vapor phase, it has been shown by Schmidt and Lee[13] that energy transfer from the benzene triplet to alkenes is fast enough to produce alkene triplets in most cases.   It is therefore noted that the triplet state of 1 produced in benzene sensitization resulted in no photoproducts.   The difference between the benzene- and mercury-sensitizations can be attributed to the triplet energy of the sensitizers, 84 and 113 kcal/mol, respectively.   The triplet state of 1 produced by mercury sensitization is considered to have a larger vibrational energy by ca. 30 kcal/mol than that produced by benzene sensitization.   Consequently, the excess vibrational energy is suggested to play a significant role in the triplet reaction.
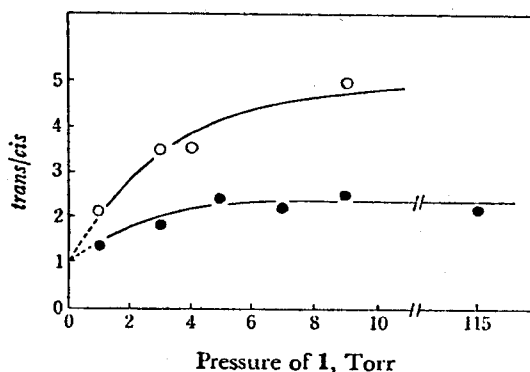
Fig. 5.   Pressure dependence of *trans-cis* ratio of 2-butene in mercury-sensitized photolysis of 1c (●) and 1t (○). Plot at a pressure of 115 Torr was obtained by adding xenon (112 Torr) to 1c (3 Torr).

The trans-cis ratio of 2-butene in the mercury sensitization of 1 was found to depend on the substrate pressure as shown in Fig. 5.   Regardless of which isomer is used, the value of the trans-cis ratio seems to approach unity at 0 torr, while it increases with increasing pressure.   The higher pressure experiment with added xenon showed that, although the trans-cis ratio decreases considerably at lower pressure (< 3 torr), the ratio is constant from 5 to 115 torr in the mercury sensitization of 1c.   An explanation of the results is found in the vibrational energy of the triplet biradical 4, this alkyl-allyl biradical being a novel instance of a "hot," triplet biradical produced in the vapor phase, although a hot, triplet biradical of the alkyl-thiyl type has recently been reported by Dice and Steer.[14]   The biradical 4 formed from 1t is considered to have a lower

vibrational energy than that formed from 1c by an anount equal to the difference in the stabilities(ΔH_f) of the two isomers, 1c and 1t.   In the absence of deactivating collisions, the hot, triplet biradical 4 has a large amount of exess vibrational energy, which renders insignificant the slight differences in the stabilities of the substrates, and therefore the trans-cis ratio approaches unity in the sensitized photolysis of 1.   At higher pressures, the difference between the energies of 4 resulting from 1c and 1t has considerable influence on the value of the trans-cis ratio.   Because of the lower vibrational energy, the biradical formed from 1t produces much more trans-2-butene than that from 1c at a comparable pressure.   These estimations explain the present results reasonably well, and also suggest that the lifetime of the biradical 4 is not long enough to be deactivated by collisions because the trans-cis ratio from 4 is still different at higher pressures.
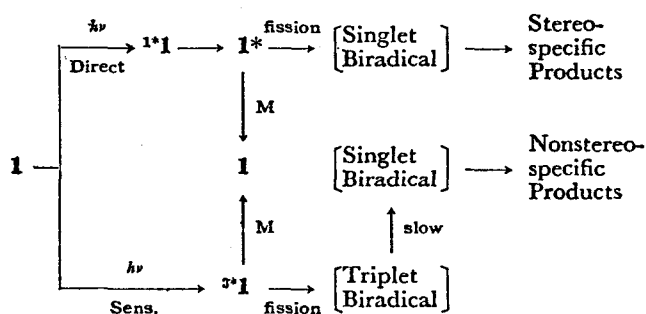
Scheme 3

The excess energy in the direct photolysis is larger by ca. 40 kcal/mol than that in the mercury sensitization, which in itself may account for the different reactivities between the direct and sensitized photolyses, since with increasing excess energy the lifetime of the intermediates should decrease favoring decomposition over rearrangement.   If this is the case, it is expected that the stereospecificity of the butene-formation in direct photolysis must decrease with increasing pressure, since collisional deactivations diminish the excess energy of the intermediates to give nonstereospecific 2-butene.   However, the trans-cis ratio of 2-butene in the direct photolysis of 1c is not affected by increasing the pressure in spite of the considerable decreases in the yields (see Fig. 2).   The rate-determining step of the direct photolysis may be the allylic C-C bond cleavage.   The different results for the direct and sensitized photolyses are, therefore,

attributed to the difference in the spin multiplicities of the intermediate involved.

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3-2 Direct and Sensitized cis-trans Photoisomerization of Cyclooctene: Effects of Spin Multiplicity and Vibrational Activation of Excited States on the Photostationary trans/cis Ratio

Photochemical cis-trans isomerization when sterically allowed is a universal photoreaction of alkenes and has been studied in considerable detail.[1] With simple alkenes where direct excitation is difficult because of weak absorption in the uv region above 230 nm,[2] triplet sensitization and the use of acyclic alkenes as substrates have been adopted in most photoisomerization studies to produce an alkene triplet state. The triplet state of an acyclic alkene thus generated, and probably the singlet state as well, is assumed to decay to the cis or trans isomer with equal probability, since the potential energy curves for the electronically excited singlet and triplet states of ethylene,[3] in which energy minima of the both excited states occur when the methylene groups are orthogonal, can be used as models for those of acyclic alkenes. As demonstrated in the vapor-phase photosensitized cis-trans isomerization of 2-butene,[4] in open-chain alkenes any vibrational excitation in the triplet state is believed to have no significant influence on the photostationary trans/cis ratio in accord with the above accepted view on the potential surface of the excited states. However, less is known of the cis-trans photoisomerization of cycloakenes with steric restrictions,[5] and the geometry and the energetics of the excited states of these molecules have not been discussed.

In this section, the auther will describe the direct and sensitized cis-trans photoisomerization of cyclooctene in the vapor and liquid phases and discuss the drastic effects of spin multiplicity of the excited states involved and of vibrational activation in the triplet state on the photostationary trans/cis ratio, which have not been observed in the photoisomerization of acyclic alkenes.

Experimental

Materials.——— Commercially available cis-cyclooctene was purified by fractional distillation through a spinning-band column and preparative glc to a purity of 99.5%. The product contained a small amount (0.5%) of cyclooctane but was free from the trans isomer.

trans-Cyclooctene was prepared by a three-step process starting from its cis isomer. The procedure consisted of performic acid oxidation of cis-cyclooctene to trans-cyclooctane-1,2-diol,[6] followed by condensation with benzaldehyde to give the acetal, and subsequent treatment with n-butyl-lithium.[7] Fractional distillation under a reduced pressure of the product gave the experimental sample of trans-cyclooctene (99.6% trans, 0.38% cis).

The sensitizers employed in the vapor- and liquid-phase photosensitization were purified by fractional distillation or recrystallization. n-Pentane was washed with concentrated sulfuric acid and then fractionally distilled.

Analysis.——— Gas chromatographic analyses of the reaction mixtures were performed using a 3 m column of 20% ODPN at 50°C or, when a sensitizer has a retention time close to that of cis- or trans-cyclooctene, a 6 m column of 15% PEG at 70°C. The cis-trans isomers of cyclooctene were separated completely under these conditions. As an internal standard, n-octane or cyclooctane was employed for the direct photolysis and the liquid-phase photosensitization.

Direct photolysis in liquid phase.——— Direct photolyses at 185 nm (as the effective resonance line of mercury) were run at 17°C using a 30 W U-shaped low-pressure mercury lamp with an immersion reactor. A pentane solution containing 0.01 M cis- or trans-cyclooctene and 0.002 M n-octane as an internal standard was flushed with nitrogen gas and then irradiated. The product distribution following the direct irradiation was determined by gas chromatographic analysis of aliquots removed from the irradiation mixture.

Liquid-phase photosensitization.——— All experiments of liquid-phase photosensitization were carried out at 17°C in a quartz or Pyrex tube, 1 cm in diameter, using a 500 W high-pressure mercury lamp. Pyrex tubing was used only for the ketone sensitizers. Pentane solutions of 0.08 M cyclooctene of a given isomer composition containing various sensitizers and 0.002 M cyclooctane or n-octane as an internal standard were flushed with nitrogen gas and then irradiated. The sensitizers are shown in Table 1 along with their concentrations employed. The isomer compositions following the uv irradiation were determined by periodic analysis of aliquots on gas chromatography. The photostationary states were obtained after prolonged irradiation; ca. 3-5 hr for the aromatics and 1-1.5 hr for the ketone sensitizers.

Vapor-phase photosensitization.——— The apparatus and the procedures employed in the vapor-phase photosensitizations were described in Chapter 2. A

mercury-free vacuum system and cylindrical quartz cells, 5 cm long and 5 cm in diameter, were used. The light source was a spiral array of a 30 W low-pressure mercury lamp fitted with a Toshiba UV-25 filter. The vapor-phase photosensitization of a given mixture (3 torr) of cis- and trans-cyclooctenes was run in the presence of the sensitizers, the pressure of which was fixed at 3 torr with benzene, fluorobenzene, benzotrifluoride, toluene, o-, m-, and p-xylene, and phenylacetylene, or at 1 torr with benzonitrile. The photostationary state was obtained for each sensitizer by repeated approach from both sides of the final composition. Control runs revealed that no detectable reactions occurred in the absence of either the uv irradiation or the sensitizers.

Results

The direct photolysis at 185 nm of a pentane solution containing 0.01 M cis- or trans-cyclooctene gave cis-trans isomerization as a major photoreaction. Moderate disappearance of cyclooctenes was observed; after 5 hr of irradiation almost half of the substrate initially used disappeared.[8] The combined yield of cyclooctenes recovered and percent of trans-cyclooctene are plotted as a function of irradiation time in Fig. 1. After prolonged irradiation, the pentane solution containing each pure isomer came to a photostationary
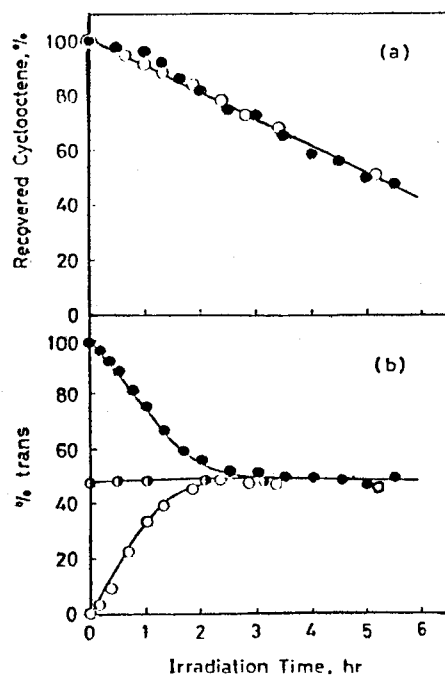

Figure 1 Combined yield (a) and percent of trans of cyclooctene on direct photoisomerization: (●) initial composition, 99.6% trans; 0.4% cis; (◑) 47:53; (○) 0:100.

state, the trans- to cis-cyclooctene ratio of which was 49:51. In order to ensure that the decomposition products did not affect the photostationary ratio, the direct irradiation of a 53:47 mixture of cis- and trans-cyclooctenes was examined under similar conditions to give the same photostationary state mixture immediately (within 30 min).

The triplet-sensitized photoisomerization of cyclooctene (0.08 M) in pentane solution was carried out in the presence of a variety of carbonyl and aromatic sensitizers (0.4 M in most cases). Regardless of the sensitizers employed, slow disappearance (2-5%/hr) of the substrate was observed. The photostationary state was determined for each sensitizer by approach from both sides of the final value. The trans/cis ratios at the photostationary state obtained for these sensitizers after prolonged irradiation are presented in Table 1 and Fig. 2. As demonstrated there, a number of

Table I: Liquid-Phase Photosensitized Cis-Trans Isomerization of Cyclooctene[a]

	Sensitizer	Concn, M	E_T, kcal/mol	$(trans/cis)_{pss}$[b]
1	Benzene	0.4	84.4	0.048
		0.04		0.047
4	Toluene	0.4	82.8	0.052
7	p-Xylene	0.4	80.4	0.047
		0.04		0.046
8	Durene	0.25	80.0	0.041
9	Benzamide	0.005	79.3	0.050
10	Benzonitrile	0.4	76.5	0.031
11	m-Tolunitrile	0.4	75.1	0.024
12	Propiophenone	0.4	74.5	0.033
13	Acetophenone	0.4	73.7	0.032
		0.04		0.030
14	4-Methylacetophenone	0.4	72.9	0.017
15	1-Tetralone	0.4	72.2	0.009
16	Phenylacetylene	0.4	72.0	0
17	Benzaldehyde	0.4	72.0	0
18	Benzophenone	0.25	6S.6	0.005
19	Fluorene	0.035	6S.0	0

[a] The concentration of cyclooctene was 0.08 M. [b] Photostationary state trans- to cis-cyclooctene ratio.
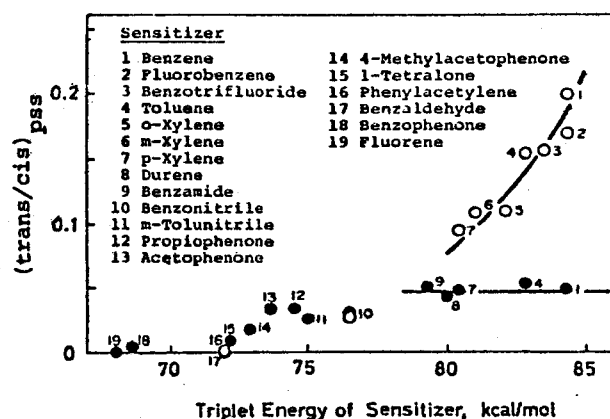

Figure 2. Variations of photostationary trans/cis ratio with triplet energy of sensitizers on vapor-phase (O) and liquid-phase (●) photosensitizations.

sensitizers with triplet energy (E_T)[9] above 72 kcal/mol are effective for the reversible cis⇌trans photoisomerization; the photostationary ratios were almost constant for the sensitizers with $E_T > 74$ kcal/mol.[10] Photo-sensitization of cyclooctene (0.08 M) by benzene, p-xylene, and acetophenone with lower sensitizer concentration (0.04 M) also gave the same photostationary ratios.

Limited experiments revealed that, although the additives with $E_T \leq 72$ kcal/mol, i.e. phenylacetylene ($E_T = 72.0$ kcal/mol), benzaldehyde (72.0), and benzophenone (68.7), failed to sensitize the cis→trans isomerization, these additives effected irreversible trans→cis isomerization; fluorene (68.0) was no longer completely effective for the photoisomerization.

Photosensitized isomerization of cyclooctene in the vapor phase was also performed in order to examine the effect of vibrational activation in the triplet state on the photostationary state. Since the sensitizers available in the vapor phase are limited by the vapor pressure, nine aromatic compounds were chosen as effective sensitizers.[11] The vapor-phase photo-sensitized isomerization of cyclooctene (3 torr) at 254 nm in the presence of sensitizers (3 torr in most cases) gave the cis-trans isomer as a major photoproduct, although prolonged irradiation led to the formation of considerable amounts of 1,7-octadiene and bicyclo[4.2.0]octane as shown in Chapter 2. The variations of the photostationary ratio with sensitizer triplet energy are shown in Table 2 and Fig. 2. The photostationary trans/cis ratio obtained in the vapor-phase photosensitization intimately depended on the triplet energy of the sensitizer used; the ratio was almost zero(more exactly trans/cis = 0.0007) at $E_T = 72.0$ kcal/mol (phenylacetylene) and then increased gradually with increasing sensitizer triplet energy in sharp contrast with the result of the liquid-phase photosensitization where the ratios were independent of the sensitizers with $E_T > 79$ kcal/mol.

Table II: Vapor-Phase Photosensitized Cis–Trans Isomerization of Cyclooctene[a]

	Sensitizer	Pressure, Torr	E_T, kcal/mol	(trans/cis)$_{ps}$[b]
1	Benzene	3.0	84.4	0.198
2	Fluorobenzene	3.0	84.4	0.163
3	Benzotrifluoride	3.0	83.4	0.156
4	Toluene	3.0	82.8	0.153
5	o-Xylene	3.0	82.1	0.111
6	m-Xylene	3.0	81.0	0.108
7	p-Xylene	3.0	80.4	0.094
10	Benzonitrile	1.0	76.5	0.026
16	Phenylacetylene	3.0	72.0	0.0007

[a] The pressure of cyclooctene was 3 Torr. [b] Photo-stationary state trans- to cis-cyclooctene ratio.

Discussion

Upon direct irradiation at 185 nm, a ground state molecule of cyclooctene is promoted spectroscopically to an electronically excited planar singlet state and then suffers fast rotational relaxation to a twisted, not necessarily orthogonal, singlet cyclooctene. Since it is believed that the large separation in energy causes excited singlet-to-triplet intersystem crossing to be very slow in such a monoolefin, the precursor of the direct cis-trans photoisomerization is inferred to be an excited singlet state of cyclooctene. The considerable disappearance of the substrate on direct photolysis suggests the existence of obscure reactions which give rise to some polymers and, if any, other uncharacterized products.[8] On the assumption of a common twisted singlet intermediate, the cis-trans photoisomerization by direct irradiation can be described by the following simple sequence:

$$c \xrightarrow{\quad h\nu \quad} {}^1p \qquad\qquad (1)$$

$$t \xrightarrow{\quad h\nu \quad} {}^1p \qquad\qquad (2)$$

$${}^1p \xrightarrow{\qquad\qquad} c \qquad\qquad (3c)$$

$$\xrightarrow{\qquad\qquad} t \qquad\qquad (3t)$$

$$\xrightarrow{\qquad\qquad} \text{Other products} \qquad (4)$$
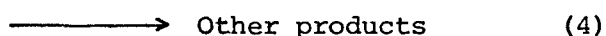
where c and t represent cis- and trans-cyclooctenes in their ground states and ${}^1p$ represents the twisted singlet cyclooctene.

A steady-state treatment of the above sequence leads to the following expression for the trans/cis ratio at the photostationary state (pss):

$$([t]/[c])_{pss} = (\varepsilon_c/\varepsilon_t)\,(k_{3t}/k_{3c}) \qquad\qquad (5)$$

where ε_c and ε_t represent the extinction coefficients of cis- and trans-cyclooctenes at 185 nm. The reported extinction coefficient for trans-cyclooctene is 5500 l/mol·cm at 185 nm,[12] while the coefficient of cis-cyclooctene was measured as 6000 l/mol·cm.[13] From these values, the excitation ratio $\varepsilon_c/\varepsilon_t$ is calculated as 1.09, and then the decay ratio can be calculated

using equation 5 and the observed photostationary ratio: $k_{3t}/k_{3c} = 0.88$.
It is worth noting that, in spite of the strain energy in the trans form
(9.3 kcal/mol),[14] an anomalously high decay ratio of 0.88 is obtained upon
direct photoisomerization.

Extremely low trans/cis photostationary ratios were observed on liquid-
phase sensitized photoisomerization: the additives with $E_T > 72$ kcal/mol were
effective for the cis $\rightleftharpoons$ trans photoisomerization. As shown in Fig. 2, a
definite photostationary ratio of 0.049 was observed for the sensitizers
with $E_T > 79$ kcal/mol, while the sensitizers in the triplet energy range 72-
77 kcal/mol give rise to somewhat lower photostationary ratios. When the
sensitizer is carbonyl compound, special regard should be paid to the inter-
mediate of the cis-trans isomerization since, as is shown in the Schenck
mechanism,[1,15] the 1,4-biradical formed by the addition of a ketone triplet
to an acyclic alkenes falls apart regenerating the alkene with geometrical
isomerization. However, in the case of ketone sensitization of cyclooctene,
such a 1,4-biradical, if formed, is considered to decompose preferentially
to the cis isomer because of the strain energy in the trans form.[14] Actually
benzophenone, which has fairly low E_T and is known to form a 1,4-biradical
with alkenes,[16] photosensitized the irreversible trans $\rightarrow$ cis isomerization
of cyclooctene, probably suggesting the predominant formation of the cis
isomer from the 1,4-biradical. It seems, therefore, likely that regarding
the ketone sensitizers with $E_T > 72$ kcal/mol, the mechanism involving triplet
energy transfer to cyclooctene is operative, although the Schenck mechanism
is applicable only for benzophenone sensitization.

Since the benzene-sensitized photostationary ratios for several acyclic
alkenes in solution are unity and the triplet energy transfer from benzene
triplet to alkenes is sufficiently exothermic,[17] it has been recognized that,
when benzene is the sensitizer, the common intermediate for the sensitized
cis-trans isomerization is the twisted alkene triplet whose decay ratio is
unity.[1,18] In the present system, assuming that the rates of energy transfer
from the excited benzene to cis- and trans-cyclooctenes are the same in ac-
cord with the above accepted view on the benzene sensitization, the extremely
low trans/cis ratio at the photostationary state is attributable to a low
decay ratio(k_t/k_c) from a common twisted, vibrationally-relaxed cyclooctene
triplet ^3p. Toluene and p-xylene sensitized photoisomerizations gave the
same, or nearly so, photostationary ratios as those obtained by benzene
sensitization, suggesting that these sensitizers with $E_T > 80$ kcal/mol also
excite both isomers of cyclooctene with an equal rate.

The calculated potential curves for the excited states of ethylene,[3] which suggest the same decay ratio for singlet and triplet excited states, are evidently unsuitable for the present system. The extremely low cis → trans isomerization efficiency for the photosensitization of cyclooctene may be attributable to a torsional conversion barrier from the vibrationally relaxed triplet state ^3p into the trans form. Taking into account the strain energy[14] and the torsional angle[19] of trans-cyclooctene in its ground state, the fundamental potential energy curves calculated with ethylene are qualitatively modified to obtain hypothetical potential curves of the ground state(N) and the excited singlet(V) and triplet(T) states of cyclooctene. Since electronically the double bond of cyclooctene is close to that of ethylene and the strain in the trans form, which arises from the steric restrictions of methylene chain, is considered not to be so great compared with the electronic energy, the potential curves for cyclooctene may not be far removed in energy from those for ethylene. Therefore, the crossing of potential curves of the N and T states occurs to give an ethylene-like energy well, although the torsional angle which give the potential minimum of the T state, and the maximum of the N state as well, should not be necessarily perpendicular. As shown in Fig. 3, a greater activation energy(E_t) is postulated for the decay of ^3p to the trans isomer in order to account for the low decay ratio in the liquid-phase photosensitization. The following Arrhenius equations are obtained for the rate constants of the
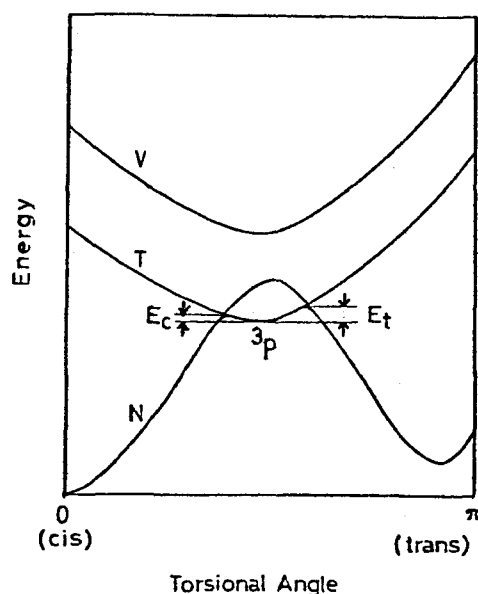

Figure 3   Schematic potential curves for the ground-state(N) and excited singlet(V) and triplet(T) states of cyclooctene.

decay from ^3p to the ground-state trans- and cis-cyclooctenes.

$$k_t = A \cdot \exp(-E_t/RT) \tag{6}$$

$$k_c = A' \cdot \exp(-E_c/RT) \tag{7}$$

Assuming the same preexponential factor, i.e. $A = A'$, the logarithm of the decay ratio is represented by the following equation

$$\ln(k_t/k_c) = - \Delta E_a/RT \tag{8}$$

where $\Delta E_a = E_t - E_c$. Since the experiment was carried out at 290°K and the decay ratio (k_t/k_c) observed equals 0.049, then the difference of the activation energy can be evaluated: $E_t - E_c = 1.7_4$ kcal/mol.[20]

The photosensitized cis-trans isomerization in the vapor phase can be used as a test of the speculated potential surface described above, since the triplet state of cyclooctene generated in the vapor-phase photosensitization is considered to have some excess vibrational energy in the absence of fast collisional deactivation by solvent molecules. As shown in Fig. 2, the trans/cis photostationary ratios observed in vapor-phase photosensitization are higher than those obtained in liquid-phase photosensitization employing the same sensitizers, and the ratio increases with increasing triplet energy of the sensitizer used, whereas the ratio observed in the liquid phase is independent of the sensitizer with $E_T > 79$ kcal/mol. One might assume the deviation from unity of the excitation ratio on the vapor-phase photosensitization in order to account for the higher trans/cis photostationary ratios and their dependence on the sensitizer triplet energy, although the excitation ratio is regarded as unity in the liquid-phase photosensitization employing sensitizers with $E_T > 79$ kcal/mol. This seems unlikely because the rates of energy transfer from benzene triplet to both cis and trans isomers of simple disubstituted alkenes have been reported to be so close in the vapor phase[4,21] that the higher trans/cis ratios observed in the present work are attributable to the higher decay ratios (k_t/k_c). The higher trans/cis photostationary ratios and their E_T dependence should therefore be interpreted in terms of the excess vibrational energy in the triplet state of cyclooctene. The cyclooctene triplet generated in the vapor-phase photo-

sensitization has some excess vibrational energy, the amount of which in-
creases with rising triplet energy of the sensitizers. According to equa-
tion 8, the excess vibrational energy, which is energetically equivalent to
thermal activation in the triplet state, enhances the the decay ratio (k_t/k_c).
Then, the enhanced decay ratio via vibrational activation qualitatively
rationalizes the higher photostationary trans/cis ratios and their dependence
on the triplet energy in the vapor-phase photosensitization. In this con-
text, the high internal energy of the relaxed singlet state ^1p in itself
may account for the anomalously high decay ratio observed on the direct photo-
isomerization. However, the auther feels prompted to propose that, since
the excited singlet state of alkenes is believed not to undergo intersystem
crossing to its triplet state but to suffer rapid internal conversion to its
ground state, the twisted ground-state cyclooctene thus formed is deactivated
collisionally to give the relaxed cis or trans isomer with almost equal
probability, if the correlation between the potential curves for the V and
N states is as shown in Fig. 3.

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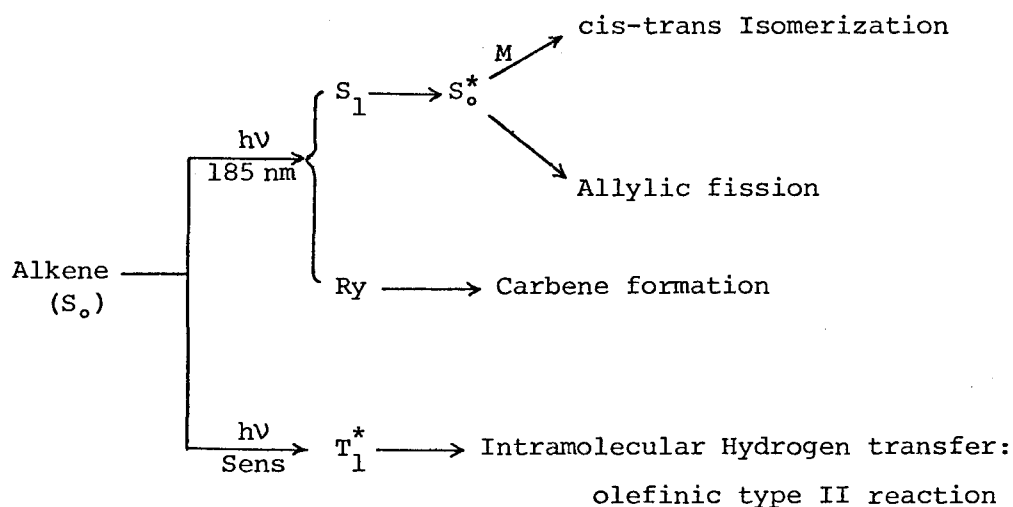
Conclusion

The principal photochemical behaviors of simple alkenes following direct and sensitized excitation were revealed in the first two chapters of this thesis. In the last chapter, two 2π-electron systems were employed in order to discuss the correlation between the electronic states involved and their reactivities.

In Chapter 1, the direct photolysis at 185 nm of simple cycloalkenes (C_6-C_9) was investigated comparatively in the vapor and liquid phases. The direct excitation promotes these simple alkenes from their ground electronic state(S_0) to the excited singlet(S_1) and Rydberg(Ry) states. It was revealed that the excited singlet of these alkenes suffers rapid internal conversion into a vibrationally-activated ground state(S_0^*) and the subsequent chemical reactions, i.e. allylic C-C bond cleavage and the cis-trans isomerization as a result of collisional deactivation. As a chemical transformation of these alkenes in the Rydberg excited state, a novel photochemical rearrangement via a carbene intermediate was found. Upon direct irradiation in the liquid phase, the highly strained trans-isomers of cyclohexene and cycloheptene were generated, and trapped at lower temperature or by acidic methanol; the lifetime of the trans-cyclo-heptene thus generated was determined at -10°C. A convenient method for preparing trans-cyclooctene was developed as a synthetic application of the direct photolysis of alkenes.

In Chapter 2, the vapor-phase photosensitization of the simple cyclic and acyclic alkenes(C_6-C_9) was investigated, and the reactivities of the vibrationally-excited triplet(T_1^*) state of these alkenes and their reaction mechanisms were discussed. On vapor-phase photosensitization, these simple alkenes underwent some novel intramolecular hydrogen transfer re-actions, which are characteristic of the vibrationally-excited triplet alkenses because of the complete suppression of these reactions on the liquid-phase photosensitization of them. Of these novel reactions, the most important primary process is the 1,5-hydrogen abstraction through a six-membered transition state resulting in a 1,4-biradical, the subse-quent β-cleavage and recombination of which provide an olefinc analogue with the Norrish type II reaction of carbonyl compounds. It was confirmed with several simple alkenes that this olefinic type II reaction is a very general and important primary process of vibrationally-activated triplet

alkenes with a γ-hydrogen.

Some of the physical and chemical processes revealed in the first two chapters may be summarized as follows.

$$
\text{Alkene } (S_0) \quad
\begin{cases}
\xrightarrow[185\text{ nm}]{h\nu} \begin{cases} S_1 \longrightarrow S_o^* \xrightarrow{M} \text{cis-trans Isomerization} \\ \qquad\qquad\quad\searrow \text{Allylic fission} \\ Ry \longrightarrow \text{Carbene formation} \end{cases} \\
\\
\xrightarrow[\text{Sens}]{h\nu} T_1^* \longrightarrow \text{Intramolecular Hydrogen transfer:} \\
\qquad\qquad\qquad\qquad\qquad \text{olefinic type II reaction}
\end{cases}
$$

In Chapter 3, the direct and sensitized photolyses were comparatively studied in order to clarify the effects of spin state and vibrational activation of the excited states involved, employing two 2π-electron systems. In the first section, the effects of spin multiplicity were discussed in the direct and sensitized photodecomposition of 4,5-dimethyl-cyclohexene vapor, the configuration of the product 2-butene being used as a probe of the stereospecificity of the reaction; the results were interpreted in terms of spin correlation effects. The intervention of a novel "hot, triplet" biradical was suggested in the vapor-phase photo-sensitization. The second section of the chapter dealt with the photo-chemical cis-trans isomerization of cyclooctene. The drastic effects of spin multiplicity and vibrational activation of the excited states involved on the photostationary trans/cis ratio were discussed and the potential energy curves for the ground state and the excited singlet and triplet states of cyclooctene which account for the present results were proposed.

The auther wishes that this thesis contributes toward more thorough and systematic understanding of the photochemistry of alkenes and other related unsaturated compounds.