

chicken tissues, eggs, and manure is reported in Table I, and that from milk and cattle tissues is reported in Table II. Figure 1 shows a recovery from 20 g of beef fat fortified with 0.1 μg of chlorfenvinphos. The final volume was 5 ml and 10 μl was injected into the chromatograph. Figure 2 shows a recovery from 20 g of chicken liver fortified with 0.5 μg of chlorfenvinphos. Final volume and injection were the same as for beef fat. As Figure 1 shows, this chromatograph did not have a switching valve to vent the solvent, and the detector was slightly more sensitive but also less stable than the detector in Figure 2.

Sensitivity. With the input attenuator at 10^3 , the output attenuator at 16, and the bucking range at 10^{-8} , 0.2 ng of chlorfenvinphos in 10 μl of hexane gave a recorder response of about 25% FSD. The control samples showed no peaks at the retention time for chlorfenvinphos. At the conditions described, 0.04 ng was readily detected and gave a response of about 5% FSD. With the sample sizes

and dilutions used, 0.001 ppm of chlorfenvinphos can be detected in the body tissues and manure and 0.002 ppm can be detected in milk. No effort was made to determine whether other phosphorous-containing compounds would interfere.

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Received for review February 5, 1973. Accepted May 2, 1973. This paper reflects the results of research only. Mention of a proprietary product or a pesticide in this paper does not constitute an endorsement or a recommendation of this product by the USDA.

Photochemical Decomposition of Heptachlor Epoxide

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The progressive decomposition of solid heptachlor epoxide (I) in KBr disks is followed by a study of the changes which occur in the infrared spectrum with time of exposure to ultraviolet radiation and sunlight. The products obtained by photodecomposition in KBr disks are identical to those obtained by exposure of solid I to sunlight and ultraviolet radiation and include a semicage ketone and an intermediate which may be converted to an enantiomeric semicage ketone. The mechanism proposed accounts for the intermedi-

ate and final products and is based upon structure determinations by infrared, nuclear magnetic resonance, mass spectrometry, and ultraviolet absorption. A study of the factors which affect the rate and extent of decomposition in the KBr solid state technique shows that the time of exposure can be controlled to produce a maximum yield of intermediate or final products. The amount of decomposition in any given sample is calculated by the absorbance ratio technique.

Heptachlor epoxide (I) is a metabolic as well as environmental oxidation product of heptachlor (Davidow and Radomski, 1953; Davidow *et al.*, 1953; Lichtenstein and Schulz, 1965; Lichtenstein *et al.*, 1970; Weatherholz *et al.*, 1967).

The metabolic and environmental decomposition products of all pesticides are important, since the toxicity of certain derivatives of polycyclic pesticides has been found to be greater than that of the original compound (Rosen and Sutherland, 1967; Rosen *et al.*, 1969). The IUPAC Commission on terminal pesticide residues makes an annual report (Egan, 1967, 1968, 1969; Hill, 1970, 1971) on this subject.

The decomposition of I has not been studied extensively. Mitchell (1961) decomposed microgram amounts of I with ultraviolet light and detected two decomposition products by paper chromatography. Banks and Bills (1968) used gas chromatography to show that I in hexane is degraded by ultraviolet light to give two compounds. Glotfelty (1972) irradiated solid I with ultraviolet light and used the resulting glc pattern for identification. None

of these investigators identified the products nor elucidated their structure. Fischler and Korte (1969) suggested a semicage structure for an isomeric photochemical derivative of I made by irradiation of I in acetone by ultraviolet light of 254 nm wavelength and Benson *et al.* (1971), in a report on chlordane photoalteration products, also suggested two possible structures. A recent article by Ivie *et al.* (1972) proposed a structure for a I intermediate photoisomer which is identical to the one (III) reported in this paper. Cochrane, in 1969, reported that basic reagents caused I to rearrange to an allylic alcohol isomer, the structure of which was elucidated by determination of the products formed by chlorination and oxidation.

This paper reports an investigation of the techniques of irradiation of solids in KBr disks and the decomposition of I by ultraviolet irradiation and by sunlight using this technique. The main derivatives are isomeric and consist of a semicage ketone and an intermediate ketone which, upon further ultraviolet irradiation, may be converted to a different semicage ketone. The photochemical degradation of I in a KBr disk is followed by a study of changes that occur in a series of infrared spectra related to time of irradiation with ultraviolet or sunlight. The residues obtained from sun-induced degradation and those obtained from the use of ultraviolet light are shown to be identical.

The structures of the derivatives shown in Figure 1 were determined by interpretation of spectra obtained from ultraviolet, infrared, mass spectrometry, and nuclear magnetic resonance instrumentation.

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Chemical Abstracts and von Baeyer names for the structures shown in Figure 1 are listed below. The first is the preferred Chemical Abstracts name for the collective index period just concluded (1967-1971) and is in line with the nomenclature rules of the IUPAC. The second name is the Chemical Abstracts index name for the present collective index period (1972-1976). The third one is the correct von Baeyer name, which is also acceptable according to the IUPAC rules. I: 1967-1971, 1,4,5,6,7,8,8-heptachloro-2,3-epoxy-3a,4,7,7a-tetrahydro-4,7-methanoindan; 1972-1976, 2,3,4,5,6,7,7-heptachloro-1a,1b,5-,5a,6,6a-hexahydro-2,5-methano-2*H*-indeno[1,2*b*]oxirene; von Baeyer, 1,3,7,8,9,10,10-heptachloro-4,5-epoxytricyclo[5.2.1.0^{2,6}]dec-8-ene. II: 1967-1971 and 1972-1976, 1,5,6,6,6a,7,8-heptachlorohexahydro-1,5:2,4-dimethanopentalen-3(2*H*)-one; von Baeyer, 1,3,7,8,9,10,10-heptachlorotetracyclo[5.2.1.0^{2,6}.0^{4,8}]decan-5-one. III: 1967-1971, 3,4,5,6,7,8,8-heptachloro-3a,4,5,6,7,7a-hexahydro-4,7-methanoindan-1-one; 1972-1976, 3,4,5,6,7,8,8-heptachloro-3a,4,5,6,7,7a-hexahydro-4,7-methano-1*H*-inden-1-one; von Baeyer, 1,5,7,8,9,10,10-heptachlorotricyclo[5.2.1.0^{2,6}]dec-4-en-3-one. IV: 1967-1971 and 1972-1976, 2,3,3,3a,4,6,8-heptachlorooctahydro-1,5:2,4-dimethanopentalen-7-one; von Baeyer, 1,5,7,8,9,10,10-heptachlorotetracyclo[5.2.1.0^{2,6}.0^{4,8}]decan-3-one.

In the following discussion, the numbers used to designate positions of carbons and hydrogens in any molecule are those shown in Figure 1, which follow the von Baeyer system.

EXPERIMENTAL SECTION

Apparatus and Reagents. A Perkin-Elmer Model 337 infrared spectrophotometer equipped with a Perkin-Elmer ir beam condenser for use with 1.5-mm KBr disks was used. A Hitachi Perkin-Elmer RMS-4 mass spectrometer equipped with a direct probe inlet at the source and a Honeywell Model 1508A oscillographic recorder were used. Both a Varian HR 220-MHz instrument and a Jeol PS-100, 100-MHz nuclear magnetic resonance instrument were used. A Barber Colman Model 5000 gas chromatograph equipped with a flame ionization detector and a 4-mm by 4-ft glass column of 8% SE-33 on 100/120 mesh Chrom Q were utilized. The carrier gas was nitrogen at 45 ml/min. The column temperature used was 220°, with the injector and detector temperatures at 240°. A high purity (99.3%) I standard was obtained from the Food and Drug Administration, Pesticide Division, Washington, D. C., in July of 1963. All solvents were ACS or distilled in glass grade.

PROCEDURES

Irradiation Conditions. Unless otherwise specified, all KBr disks were 0.5% w/w (1.00 mg of I in 200 mg of KBr) and were irradiated with 254 nm radiation at a distance of 4 in. from the uv lamp on aluminum foil. The disks were inverted after each exposure so that opposite sides were exposed alternately. In some studies, the disks were fixed in position on holders in such a manner that either side could be exposed and the holders were inverted after each irradiation period. In most cases, infrared spectra were determined immediately after exposure.

Study of Disk Orientation. A disk which had been irradiated for 200 hr was marked and successive infrared spectra were determined after rotating the disk 90° between scans. The absorbances of several wavelength bands in the four positions were compared to determine the homogeneity of the disk and the effect of the position of the disk in its support.

Shielding Effect Studies. Three KBr disks of I were exposed simultaneously for various periods of time, with one being covered by a blank KBr disk, a second being

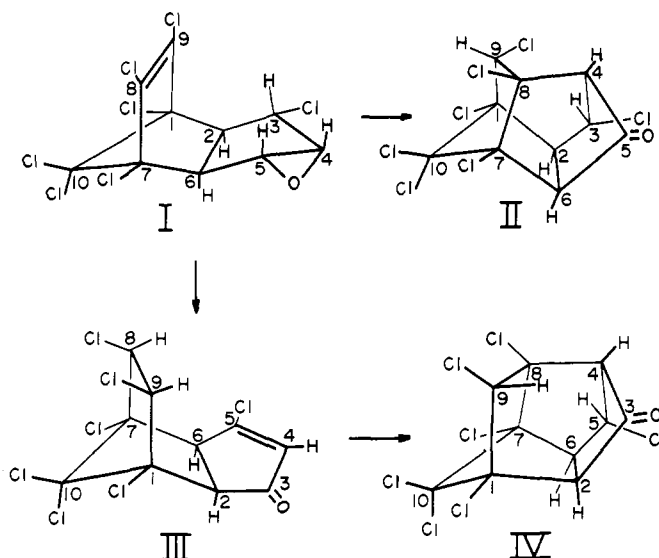


Figure 1. Structures of I-IV.

covered with a 1% disk of I, and the third being uncovered.

Effect of Elevated Temperatures on Degradation. KBr disks of I were held at elevated temperatures for extended lengths of time and checked periodically by infrared spectroscopy. A 0.3% disk of III in KBr was heated for extended periods at successively higher temperatures.

Study of the Effect of the Physical Condition of I during Exposure. A disk of I in KBr, a compressed disk of 200 mg of pure I, and a sample of powdered I were sealed in separate quartz tubes and irradiated for various periods of time: 19 hr for the KBr disk; 23 hr for the I disk; and 84 hr for the powder sample.

Sun-Induced Degradation. A second series of similar samples of I in KBr, compressed I, and I powder were sealed in quartz tubes and exposed continuously over aluminum foil for 121 hr during July of 1970 on the roof of a building in a position which was not shaded during any portion of the day. A second powder sample of I was exposed under the same conditions for 23 days during August of 1970. A third powder sample of I was exposed continuously from Dec 31, 1969, to Sept 10, 1970, with portions being removed periodically after thorough mixing for infrared spectra determination.

Ultraviolet Light-Induced Decomposition. A 0.35% w/w I KBr disk was fixed in position on a holder and irradiated for various consecutive time intervals, with the infrared spectrum being determined after each exposure. Intervals used were 1 hr for the first 20 hr, 2 hr for the next 20 hr, 4 hr for the next 40 hr, and longer nonuniform intervals for the next 72 hr. The disk was stored in a desiccator in the dark between exposures. After extended storage (overnight or over weekend), the infrared pattern was rerun before starting the next irradiation period. No change was noted during any storage period. These data were used as the basis of the proposed method to determine the extent of decomposition in I standards by the absorbance ratio technique (Graham and Kenner, 1969).

Proposed Method for Determination of the Extent of Decomposition in I Standards. Prepare an approximately 0.5% disk of I in KBr and run the infrared spectrum. Measure the net absorbances at 1600 and 1775 cm^{-1} using a straight line drawn from the curve at 1350 cm^{-1} to the curve at 1900 cm^{-1} as a common baseline. Divide the net absorbance at 1600 cm^{-1} by the net absorbance at 1775 cm^{-1} to obtain the absorbance ratio. Read the per cent undecomposed I from a graph of absorbance ratio *vs.* per cent undecomposed sample, obtained by plotting the data in the ultraviolet-induced decomposition study in Table I.

Table I. Absorbance Ratios and Per Cent of Undecomposed I

% undecomposed I	Absorbance ratio	
	A1600 cm ⁻¹ /A1775 cm ⁻¹	A690 cm ⁻¹ /A1775 cm ⁻¹
100	124.7	97.7
99.9	96.5	75.5
99.5	50.5	39.6
99.0	31.6	24.7
98.5	22.9	17.9
98.0	17.9	14.0
97.0	12.5	9.72
96.0	9.49	7.41
94.0	6.37	4.97
92.0	4.75	3.70
90.0	3.75	2.92
88.0	3.08	2.39
86.0	2.60	2.01
84.0	2.23	1.72
80.0	1.71	1.32
60.0	0.667	0.498
40.0	0.314	0.222
20.0	0.137	0.0834
10.0	0.0775	0.0371
5.0	0.0526	0.0176
0	0.0302	0

If desired, the data for the absorption at 690 cm⁻¹ or other wave numbers may be substituted for the 1600 cm⁻¹ data.

Gas-Liquid Chromatography, Quantitation, and Trapping Procedures. In all gas-liquid chromatographic quantitation and trapping procedures, the KBr disks containing the decomposition products were ground, placed in an 8-mm chromatographic column, and eluted with chloroform, the chloroform was evaporated and the residue weighed. For quantitation, the residue was dissolved in sufficient chloroform to give a concentration of approximately 1 mg/ml and analyzed by gas chromatography, using heptachlor as an internal standard. For trapping procedures, the residue was dissolved in the smallest feasible amount of chloroform and the separated products were trapped sequentially in melting point tubes attached to a heated exit port of the gas chromatograph by repeated injections of small aliquots. Samples of each decomposition product were also trapped in melting point tubes which contained powdered KBr. After trapping, the KBr was extruded to allow preparation of micro (1.5-mm diameter) disks which were scanned to obtain the infrared spectrum of each individual product.

Preparation of Samples for Structure Studies. Individual samples of II and III were obtained by irradiation of 50 KBr disks of I for 10 hr, or until the optimum amount of III was present. The disks were ground, extracted, chromatographed, and trapped by the usual procedure. A pure sample of IV was prepared by irradiation of portions of III obtained from the irradiation of I. In this procedure III was dissolved in chloroform which was evaporated in the presence of KBr to allow preparation of disks. Infrared spectra were made and the disks irradiated for six 5-min intervals, four 10-min intervals, and then for longer but varying intervals for 255 min, to make a total of 325 min of irradiation, at which time the conversion to IV was complete, as shown by the infrared spectra made after each irradiation period. The disks were ground, mixed, placed in an 8-mm column, eluted with chloroform, and the chloroform was evaporated.

A relatively larger sample of II needed for nmr studies was prepared by simultaneous irradiation of 120 KBr disks of I for 81 hr or until the infrared spectrum indicated that essentially no I or III was present. The disks were ground, placed in an 8-mm column, eluted with chloro-

form, and the chloroform was evaporated. The resulting brown residue was extracted with successive small volumes of chloroform which dissolved only a portion of the material. The infrared spectrum of the compound obtained by the evaporation of these combined extracts showed no peaks attributable to IV.

Structure Studies. *Ultraviolet.* Samples of I-III were dissolved in either methanol or chloroform and scanned in the ultraviolet region. Molar absorptivity values were calculated.

Mass Spectrometry. Individual solid samples of I-IV were placed in the capillary cup of the direct probe inlet assembly and inserted into a heatable chamber very near the ion source. The temperature of the sample was gradually increased, while monitoring the ion current produced as the sample vaporized. In each case, the spectrum was recorded at 70 eV when the ion current was at its maximum.

Nuclear Magnetic Resonance. The nmr spectra of I-III were obtained against tetramethylsilane on a 220-MHz spectrometer using CDCl₃, CCl₄, C₆D₆, and 40:60 C₆D₆:C₃D₆O as solvents. The nuclear Overhauser effect experiment and very high resolution spectra were obtained from a 100-MHz spectrometer.

RESULTS AND DISCUSSION

Since the use of infrared spectra to follow the course of changes caused by irradiation and/or temperature on solid substances in KBr disks has not been studied extensively, several parameters were investigated to determine the most effective method of irradiation. Because the beam in the Perkin-Elmer Model 337 infrared spectrophotometer does not pass through the center of the disk, slight inhomogeneities in thickness or distribution of the radiation sensitive material can cause variations in the measured absorbance of individual peaks. In a test of a disk which has been irradiated until no further change was apparent in the spectra, rotation of the disk by 90° caused as much as a 7% change in the absorbance of key bands. As a consequence, the disk must be fixed in position in the holder so that the same portion of the disk is scanned each time the infrared spectrum is run. This is especially necessary when spectra are to be determined after each irradiation to follow a given decomposition by the absorbance ratio method which compares simultaneous changes in two absorption bands.

The effect of decreasing the intensity of radiation by shielding the exposed disk with other disks shows that the uncovered disk decomposes at approximately ten times the rate of a disk covered with a blank KBr disk and approximately 140 times the rate of a disk covered with a KBr disk containing 1% of I.

There is no evidence of decomposition of I due to elevated temperatures even though one disk was held at 35° for a period of 322 days and other disks were held at 120° for 197 hr. The heat stability of III is shown by the fact that the infrared spectrum of a disk of III which was heated for various times at various temperatures, beginning with 35° for 29 days and ending with 105° for 8 days, showed no apparent change.

The physical condition of the solid has an effect upon the rate of light-induced decomposition whether the radiation is by ultraviolet lamp or by sunlight. A 0.5% disk of I in KBr decomposes more rapidly than a disk of pure I which, in turn, decomposes more rapidly than powdered I. The results of continuous periods of exposure of these three types of samples are shown in Table II. The extent of decomposition was calculated by the absorbance ratio technique. This study also indicates that 121 hr of continuous exposure during a sunshiny period in July of 1970 was not as effective in KBr disks as 20 hr of exposure to uv light in the Chromato-Vue, but that exposure of the

Table II. Effect of Physical Condition of Sample on Rate of Decomposition

	Irradiation by			
	Outdoor exposure, July 1970		254 nm uv	
	Hours continuous exposure	Undecomposed I remaining	Hours continuous exposure	Undecomposed I remaining
KBr disk 0.5% I	121	Zero ^a	20	90.6
Solid disk of I	121	92.8	23	99.5
Powdered HE	121	98.7	84	98.8
Powdered HE	557	40.7	N.D. ^b	N.D. ^b

^a The infrared spectrum of the disk indicated that no I was left undecomposed. ^b N.D., not determined.

powder during this same period for a little over 23 days caused more than 50% decomposition.

Another sample of I powder was exposed on a roof continuously from Dec 31, 1969, through Sept 10, 1970, with the results shown in Table III. The rate of decomposition was almost negligible until May and then increased rapidly through July. During July the rate of decomposition was approximately 1% per day. These studies indicate that I is decomposed by sunlight and ultraviolet radiation and that the rate of decomposition when exposed to the atmosphere is dependent upon the amount of sunshine striking the sample and the physical condition of the sample.

In order to follow decomposition of irradiated or heated samples, infrared spectra were run after each exposure and compared to determine which bands were decreasing, appearing, and/or increasing. Portions of the infrared spectra of a KBr disk of I taken after stated intervals of exposure to 254-nm ultraviolet radiation are shown in Figure 2. The absorbances of the bands at 1600, 1385, 1167, 908, 857, 690, and 674 cm^{-1} decrease continually during exposure to a minimum and may be used to represent the amount of undecomposed I remaining in the sample. The absorbances of the new bands at 1775 and 1380 cm^{-1} continually increase to a maximum during exposure, and may be used to represent the increasing amounts of II being formed during decomposition. The bands at 1717 and 1577 cm^{-1} , which do not occur in the spectrum of I, increase during the first portion of the radiation period and then decrease to a minimum with extended exposure. These bands represent the formation of III and its subsequent conversion to IV. The 1745 cm^{-1} band, which is due to IV, does not appear until the 1717 cm^{-1} band, due to III, begins to decrease. A typical example of the variation of absorbance with time of irradiation for certain of these peaks is shown in Figure 3, and the baselines used to calculate net absorbances are shown in Table IV. As shown by the decreasing bands, the rate of decomposition is essentially constant for the first 20 hr and then decreases with increasing time of exposure. The I is apparently completely decomposed in 35 to 42 hr, since the absorbance of the decreasing bands becomes constant after this exposure time. However, the absorbance of the bands associated with II continues to increase until it becomes constant at approximately 65 hr exposure time. During the period from 20 to 80 hr the absorbance of the bands due to III decreases from the maximum at approximately 15 hr to a minimum. Similar changes have been noted in several different samples irradiated over various periods of time. In every case, the first new band to appear upon radiation was the carbonyl band of III at 1717 cm^{-1} , the second was the carbonyl band of II at 1775 cm^{-1} , and the third was the double bond band due to III at 1577 cm^{-1} . The first

Table III. Sun-Induced Degradation of I

Date	% I undecomposed	No of days of continuous exposure between ir scans	Rate of decomposition during period of exposure, % per day
12-31-69 (start)	100	0	
1-8-70	99.8	8	
5-15-70	93.1	127	0.053
6-8-70	91.1	24	0.083
7-8-70	88.5	30	0.087
7-21-70	78.0	13	0.81
7-31-70	68.0	10	1.00
8-10-70	66.0	10	0.20
9-10-70 (end)	61.0	51	0.098

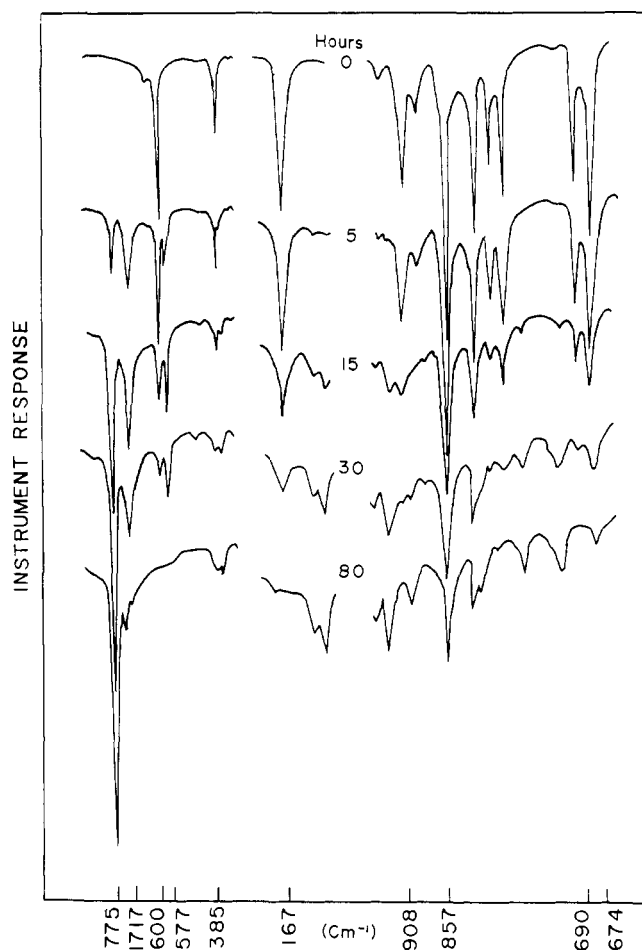


Figure 2. Infrared spectra of I after various periods of irradiation by uv light.

band appeared in less than an hour, the second at about one hour, and the third after approximately 2 hr of irradiation.

The data from Figure 3 were used to obtain the relationship between the absorbance ratios and extent of decomposition shown in Table I and in Figure 4 by the absorbance ratio method (Graham and Kenner, 1969). An expanded portion of the graph for the absorbance ratio 1600 cm^{-1} :1775 cm^{-1} from 80 to 100% was used to determine the percentage of undecomposed I remaining after any particular exposure in this study. The data from Table I can be used to construct similar graphs which can be used with the infrared spectrum from any infrared instrument to estimate decomposition in I standards or samples, since use of the absorbance ratio between in-

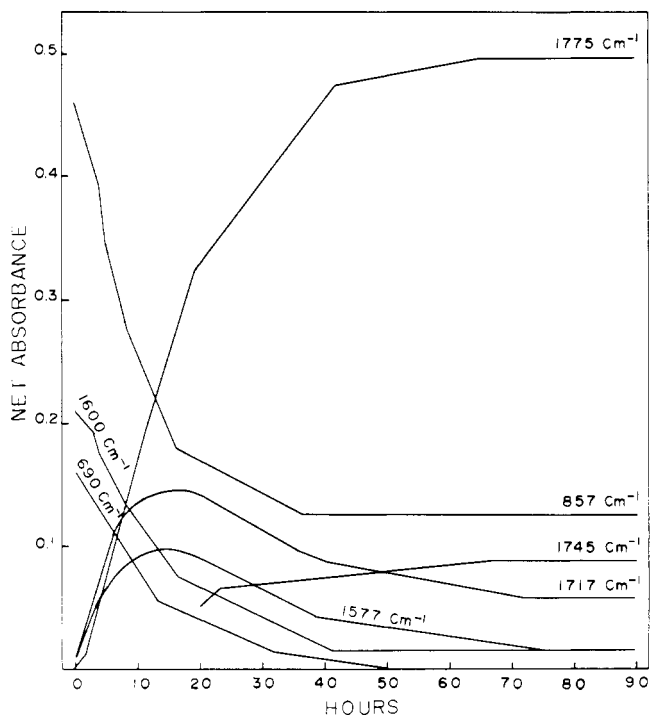


Figure 3. Variation of absorbance of ir bands with time of irradiation by uv light.

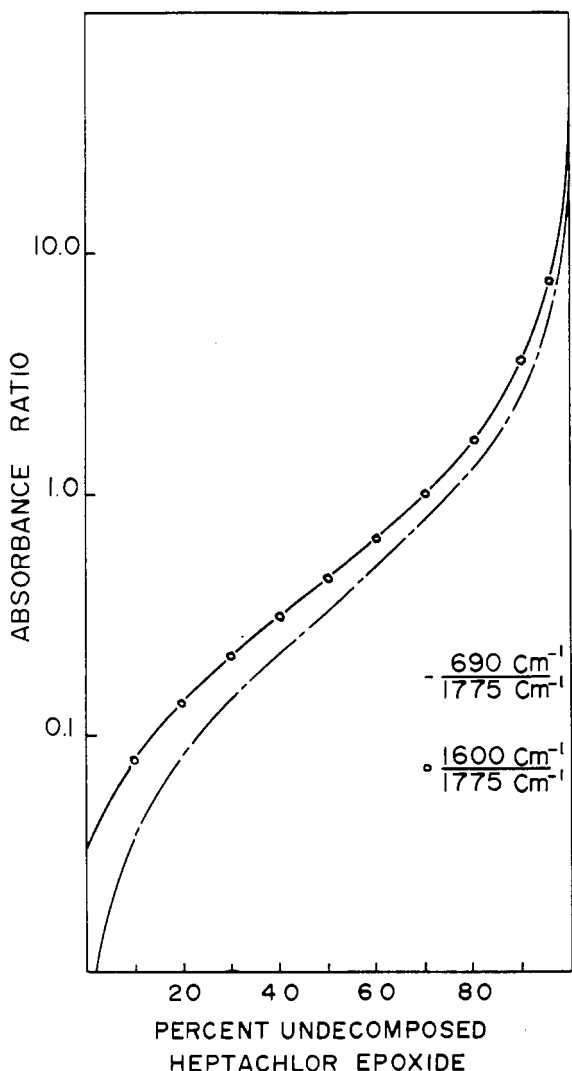


Figure 4. Variation of absorbance ratios with per cent undecomposed I.

Table IV. Base Lines Used for Absorbance Measurements

Absorbance peak, cm^{-1}	Draw base line	
	From, cm^{-1}	To, cm^{-1}
1775, 1600, 1577, 1385	1350	1900
1167	1150	1200
908	880	980
857	835	875
690, 674	650	750

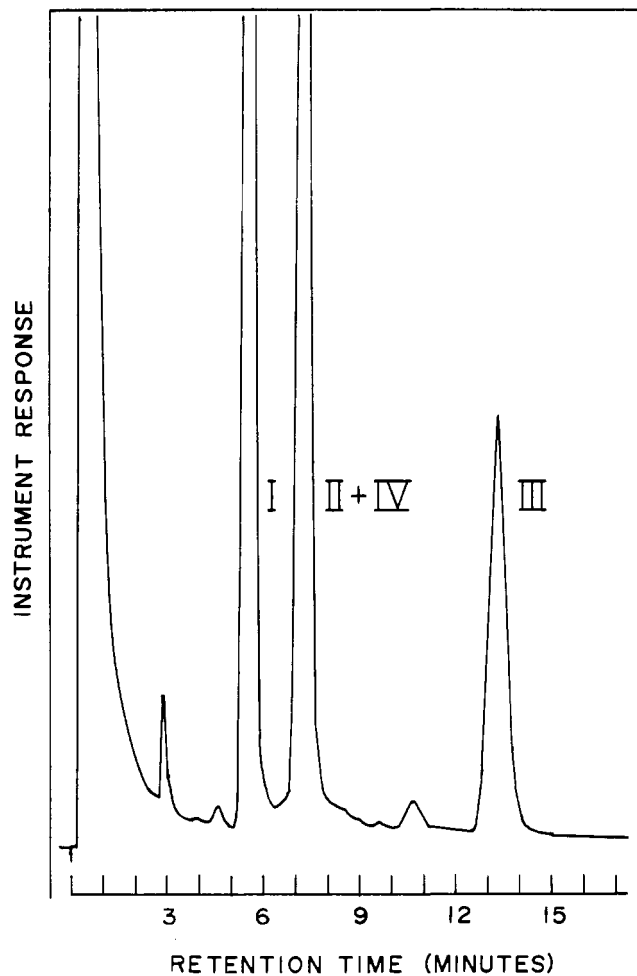


Figure 5. Glc spectrum of partially decomposed I.

frared bands in the same spectrum offsets instrumental, concentration, and disk thickness variables (Graham and Kenner, 1969).

The glc spectrum of a sample which contained 43% undecomposed I is shown in Figure 5 as a typical chromatogram of partially decomposed I. The three main peaks due to I, II, and III have relative retention times (compared to I) of 1.00, 1.31, and 2.40, respectively. Three minor peaks which were not identified have relative retention times of 0.52, 0.83, and 1.93 and account for approximately 2% of the total mass area. The peak due to II probably contains IV, since both substances have identical retention times on this column and on a polar column (4% JXR). Prepared mixtures of II and IV also gave a single peak on both columns.

The extent of decomposition in several samples was determined by glc using heptachlor as an internal standard and also by the infrared absorption ratio method. One of the powder samples which had been exposed to sunlight was found to average 19.2% decomposition by duplicate glc runs and 17.5% by the absorbance ratio technique. Another powder sample which had been irradiated by uv

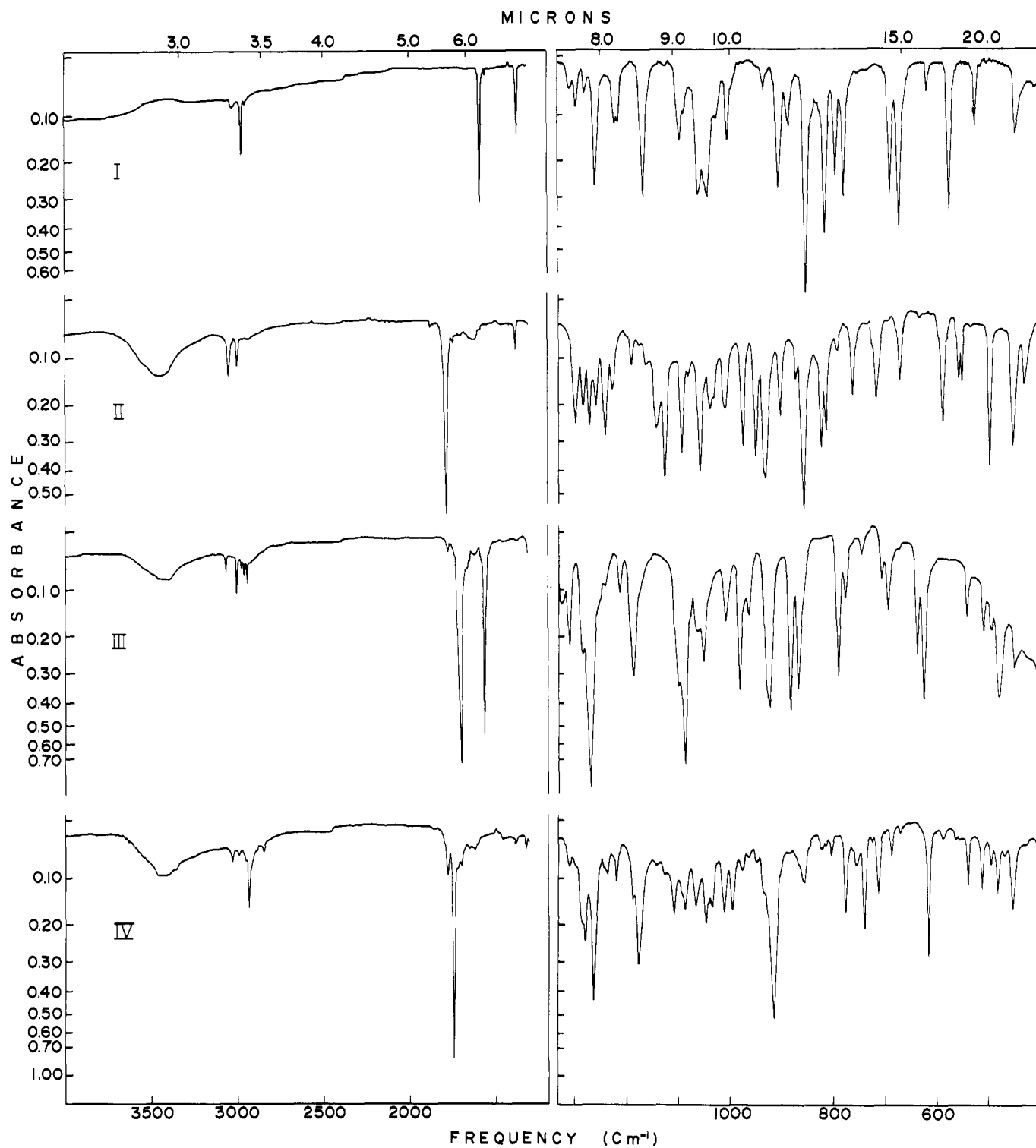


Figure 6. Infrared spectra of I-IV.

averaged 8.3% decomposition by duplicate glc runs and 6.0% by the absorbance ratio method. These results are typical of many samples which were analyzed and illustrate the satisfactory agreement between the two methods.

The infrared spectra of I and its decomposition products which were trapped from the gas-liquid chromatographic column are shown in Figure 6. The spectra of the products obtained by ultraviolet irradiation are identical to the spectra of those obtained by exposure to sunlight and the spectrum of the unconverted trapped I is identical to that of the original I. Trapped II was a white crystalline solid, while trapped III appeared to be a liquid which later crys-

tallized as a solid with a refractive index approximately that of the glass melting point tube.

The conversion of III to IV by irradiation after separation of III by glc trapping from the other decomposition products was monitored by following the decreasing absorbance of the bands at 1570 and 1700 cm^{-1} , which represent the decreasing amount of III, and the increasing absorbance of the bands at 611 and 1745 cm^{-1} , which represent the increasing amount of IV. The variation of the absorbance of these bands with time of irradiation is shown in Figure 7. Approximately 60% of the original weight of III was recovered as IV. There was no indication in the infrared spectrum that any II was formed when III

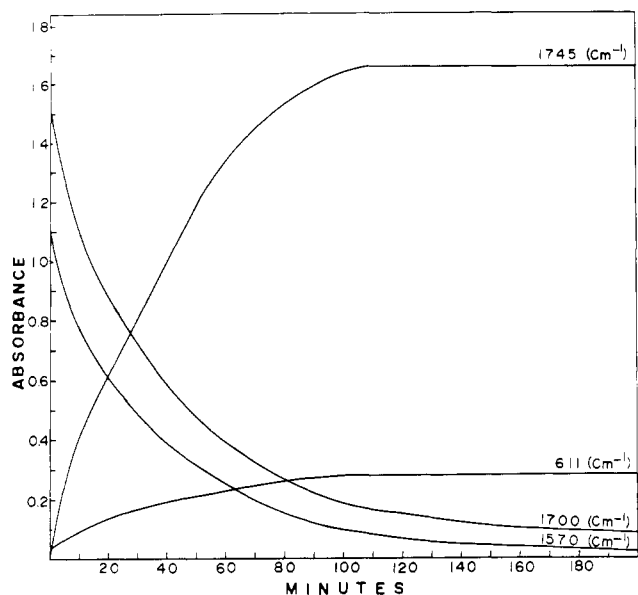


Figure 7. Variation of absorbance of ir bands of III being converted to IV with time of irradiation by uv light.

was converted to IV. The ultraviolet spectrum of III in methanol shows a strong absorption band at 234.5 nm, which has a molar absorptivity of 4700. This wavelength is correct for a double bond which is in conjugation with a carbonyl in a cyclopentene ring (Cochrane, 1969; Silverstein and Bassler, 1967). II in chloroform shows an ultraviolet absorption band at 297 nm with a molar absorptivity of 24, which is characteristic of an $n \rightarrow \pi^*$ transition for an isolated carbonyl.

The infrared spectra furnish information concerning sequential molecular structural changes with time of irradiation and also give some indication of the structural characteristics of the decomposition products of I. There is only one oxygen atom in I but two carbonyl groups are indicated by the bands at 1775 and 1717 cm^{-1} , which appear in the composite spectrum of partially decomposed I. As a consequence, at least two decomposition products of I are present in the partially decomposed sample.

The absorption band at 1775 cm^{-1} in the spectrum of II, which is used in this study to follow the formation of II, is the result of a strained carbonyl (Nakanishi, 1964). The strain is probably caused by the carbonyl being incorporated into two fused five-membered rings, which indicates semicage structure II. Also the general appearance of the fingerprint region of the spectrum with many narrow sharp bands is like that of other semicage chlorinated pesticides such as photodieldrin (Klein *et al.*, 1970).

The infrared spectrum of III trapped from a gas-liquid chromatograph shows a carbonyl absorption band at 1700 cm^{-1} and a double bond absorption band at 1570 cm^{-1} which are almost equal in intensity. This is typical of an "S" cis double bond which is located α, β to a ketone (Nakanishi, 1964). There is also a band at 1260 cm^{-1} due to a chlorine and a hydrogen on the same secondary carbon atom, as well as a carbon stretching and bending band at 1081 cm^{-1} due to the $-\text{CC}(=\text{O})\text{C}-$ grouping (Silverstein and Bassler, 1967). The carbonyl band at 1700 cm^{-1} and the double bond band at 1570 cm^{-1} are related to each other since both increase to a maximum and then decrease with approximately the same difference in absorbance at any given time of irradiation past optimum absorbance until both disappear. The difference in absorbance of these two lines for a typical disk averages 0.065 absorbance units for each milligram of I during the radiation period in which the absorbance of these lines is decreasing.

The absorption band at 1745 cm^{-1} in IV spectrum shows a less strained carbonyl than the absorption band at 1775 cm^{-1} in II and indicates that the carbonyl may be contained in a five-membered ring fused to a six-membered ring rather than the two fused five-membered rings in II. There is a doublet at 1264 cm^{-1} and a peak at 1250 cm^{-1} in the spectrum of IV which are caused by a chlorine and hydrogen atom on the same secondary carbon atom.

The main differences between the spectrum of III and the spectrum of IV formed by irradiation of pure III include the fact: that there is no double bond at 1570 cm^{-1} in the spectrum of IV; that the carbonyl band has a value of 1745 cm^{-1} in IV and 1700 cm^{-1} in III; that the peak at 1264 cm^{-1} which occurs in both spectra is twice as strong in the spectrum of III as it is in the spectrum of IV; and that the stretching and bending band at 1081 cm^{-1} in III spectrum appears at 1165 cm^{-1} in the IV spectrum. The shift of the carbonyl and/or the stretching and bending bands to higher wavelengths indicates that the increased strain in the structure of IV may be caused by the loss of conjugation due to the disappearance of the double bond. The disappearance of the double bond band together with the decreased intensity of absorption at 1264 cm^{-1} indicates the formation of a bridge utilizing the double bond and a secondary carbon to which both hydrogen and chlorine are attached. All of these differences point to the formation of semicage structure IV.

Infrared spectra of decomposition mixtures of I show the carbonyl of III at 1717 cm^{-1} and the double bond at 1577 cm^{-1} , whereas the spectrum of pure III shows the same bands at 1700 and 1570 cm^{-1} , respectively.

Mass Spectrometry. The mass spectra of I-IV are shown in Figure 8. The spectrum of I has been published (Damico *et al.*, 1968) and is included here only to show agreement and to allow direct comparison with the decomposition products. The mass spectra show the four compounds to be isomeric with a molecular weight of 386 and all having major peaks for the $(\text{M} - \text{Cl})$ ion. The mass spectrum of each is different, with that of III being the most complex. At least seven different fragmentation routes can be outlined for the higher mass portion of this spectrum. Both II and IV show a single major fragmentation route with the loss of a chlorine atom followed by a CO fragment and then three molecules of HCl to give major m/e peaks at 351, 323, 287, 251, and 215, respectively. From m/e 386 down to 150 the fragmentation pattern for IV is almost identical to that of II, except for small changes in relative intensities. Below m/e 150 the patterns differ significantly.

Nuclear Magnetic Resonance. The 220-MHz spectra of I-III are shown in Figure 9. The chemical shifts and coupling constants are given in Table V. Field decoupling was performed where needed for proton identification.

The nmr spectrum of III shows that H_2 and H_6 are coupled to each other ($J = 8.4$ Hz), with H_2 being the most deshielded. H_6 is additionally coupled through the double bond to H_4 with $J = 1.6$ Hz. The chemical shift of H_4 , deshielded because of its location, is close to the value of 6.3 ppm reported for 1-keto-3-chlorochlordene (Cochrane, 1969). H_8 is shielded less than H_9 by the carbonyl, since it is perpendicular to the carbonyl. This coupling ($J_{8,9} = 8.7$ Hz) is consistent with a cis orientation of H_8, H_9 but trans cannot be completely ruled out. Since the nmr spectrum elucidates the positions of the protons in the molecule, the data obtained from uv, ir, and mass spectrometry can be used to assign the structure shown in Figure 1.

The nmr spectrum of II is more complex and more difficult to interpret than that of III. Integration of the spectrum obtained in C_6D_6 shows one proton at each of five different chemical shifts. This spectrum indicates that H_9 is the most deshielded proton and is a singlet due to the

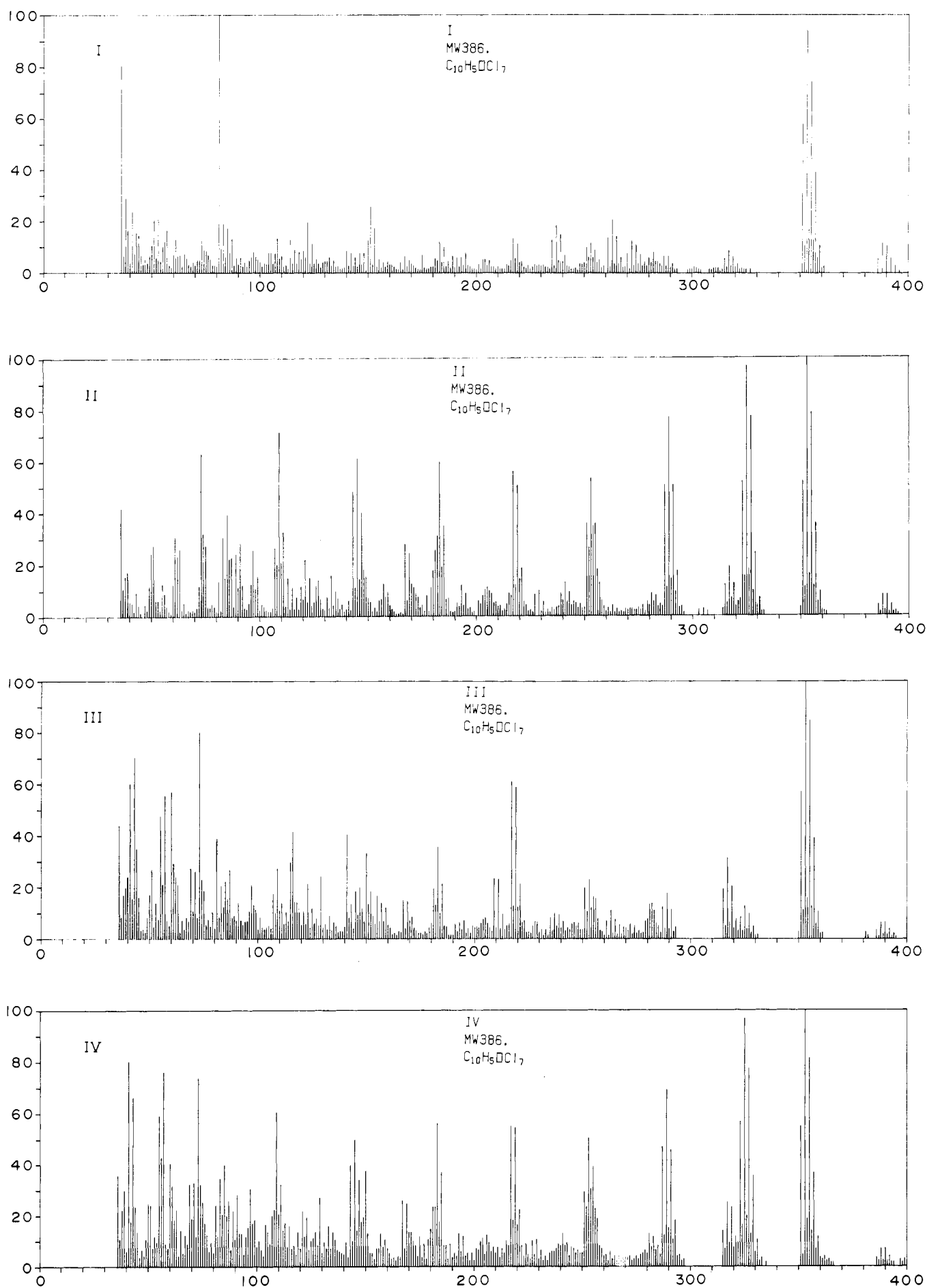


Figure 8. Mass spectra of I-IV.

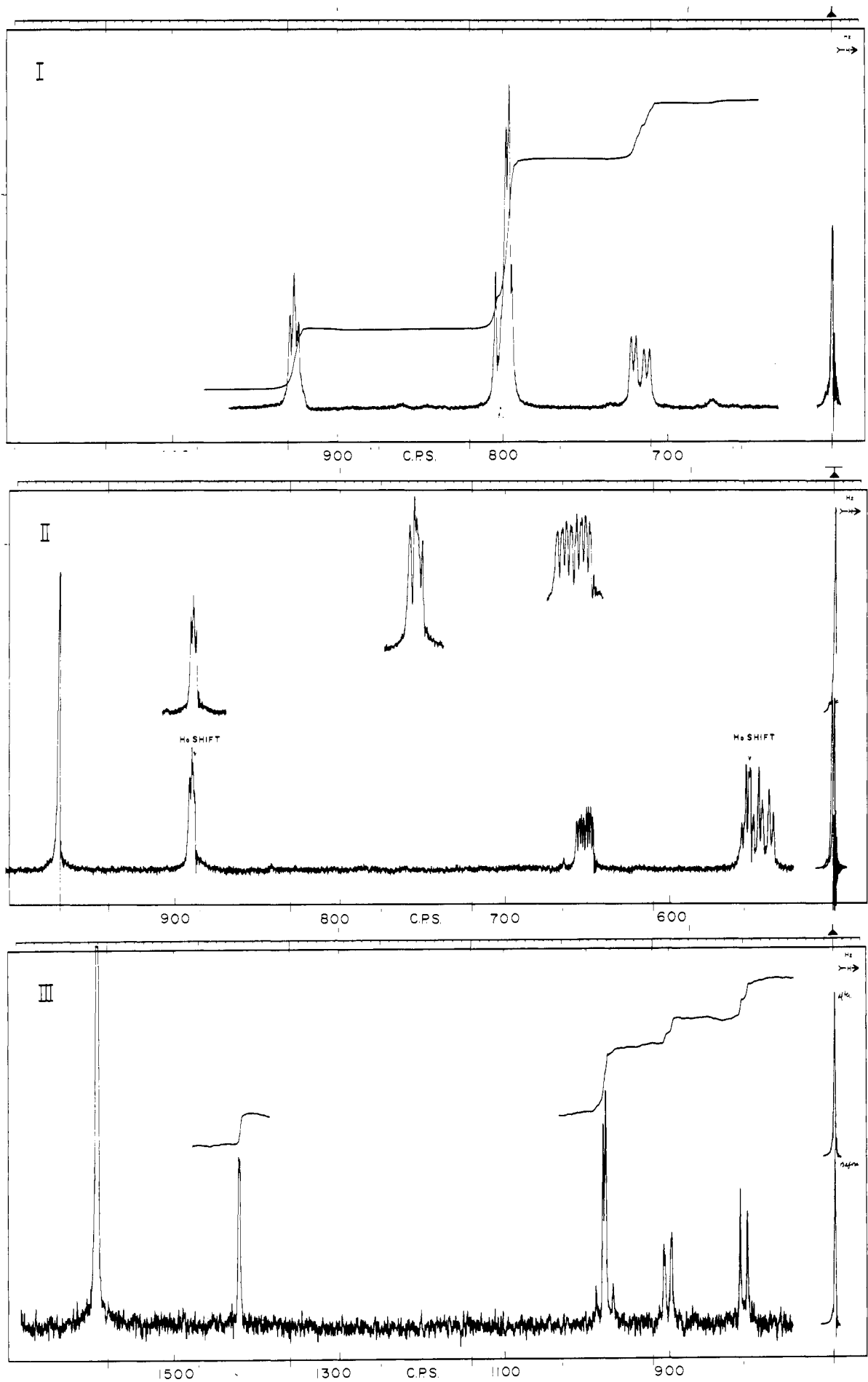


Figure 9. Nmr spectra of I-III at 220 MHz.

Table V. Nmr Coupling Constants and Chemical Shifts for I and its Photoisomers

Proton no.	Chemical shift, ppm ^a	Description of peak	Coupling constant, Hz
II in C ₆ D ₆			
H ₆	2.466	Doublet of doublets	$J_{4,6} = -2.24$
H ₄	2.511	Quartet	$J_{2,6} = +5.96$
H ₂	2.961	Doublet of doublet of a doublet of doublets (ABMX system)	$J_{3,4} = +2.20$
H ₃	4.041	Doublet of doublets	$J_{2,4} = +2.57$
H ₉	4.405	Doublet	$J_{2,3} = +1.68$ $J_{2,9} = +0.32$
III in C ₆ D ₆ ^b			
H ₂	3.686	Doublet	$J_{2,6} = +8.4$
H ₆	4.114	Doublet of doublets	$J_{4,6} = -1.6$
H ₉	4.437	Doublet	$J_{3,9} = +8.7$
H ₈	4.469	Doublet	$J_{5,9} = +8.7$
H ₄	6.472	Doublet	$J_{4,6} = -1.6$
I in CCl ₄ ^b			
H ₂	3.255	Doublet of doublets	$J_{3,4} = +1.8$
H ₄ , H ₅	3.61-3.62	AB system	$J_{4,5} < 1.3$
H ₆	3.643	Doublet	$J_{2,6} = +7.5$
H ₃	4.207	Doublet of doublets	$J_{2,3} = +2.8$

^a Relative to TMS. ^b Assumed signs of J 's.

semicage structure and deshielding by the chlorine atom on the same carbon. However, a high resolution spectrum at 100 MHz showed the H₉ peak to be a doublet ($J = +0.32$ Hz). The splitting pattern for H₂, H₄, and H₆ is found on analysis to be due to long range and regular coupling between them. H₂ is split by H₆ ($J = +5.96$ Hz), H₃ ($J = +1.68$ Hz), H₄ ($J = +2.57$ Hz), and H₉ to give a 16-line multiplet or a doublet of doublet of a doublet of doublets located at 2.96 ppm. H₃ is more deshielded and is split by H₄ ($J = +2.20$ Hz) and H₂ ($J = +1.68$ Hz) to give a distorted triplet which appears at 4.04 ppm. H₆ is the most shielded of the protons and couples with H₂ ($J = +5.96$ Hz) and by long range coupling with H₄ ($J = -2.24$ Hz) to yield the doublet of doublets observed at 2.466 ppm. Also the similar magnitudes of $J_{2,4}$, $J_{4,6}$, and $J_{3,4}$ indicate that H₄ is a quartet. The data obtained by using average values for line frequencies obtained by analysis of repetitive scans on the nmr using 250-Hz scale and a 250-second sweep speed were analyzed and iterated with a Laocoon III computer program. The curves were plotted for all possible arrangements of signs of the coupling constants for $J_{2,4}$ and $J_{4,6}$ for the four protons at H₂, H₄, H₆, and H₃. The resulting bar graph, which is characteristic of an ABMX system (where $J_{2,9}$ was neglected), fits the experimental results for $J_{4,6} = -2.3$ Hz and $J_{2,4} = +2.6$ Hz. This shows that the bridge side of the cage structure of II has a $-J$ long range coupling, while the open side has a $+J$ long range coupling.

The nmr spectrum of II was also run in CDCl₃. The chemical shifts of each proton compared with those in C₆D₆ are shown in Table VI. The large difference in chemical shifts for the same protons in the two solvents indicates that benzene is solvating the carbonyl of II. It shows that H₆ and H₄ are closest to the benzene ring and are shielded the most, while H₂ and H₃, which are farther away, are shielded less. H₉ is not only farthest away, but is also not directly over the benzene ring and is the least shielded. The solvation effect is verified by comparison of the chemical shifts produced by the addition of D₆ acetone to C₆D₆ in a 60:40 ratio. The resulting chemical shifts of the protons of II in this solvent (Table VI) are closer to those found in CDCl₃ because of the competition of the carbonyl of the D₆ acetone for the C₆D₆. Note that

Table VI. Chemical Shifts Due to Solvent Effect on II

Solvent	Chemical shifts				
	H ₆	H ₄	H ₃	H ₂	H ₉
CDCl ₃ ^a	3.205	3.261	4.723	3.656	4.727
C ₆ D ₆ ^a	2.466	2.511	4.041	2.961	4.405
Δ ppm	0.739	0.750	0.682	0.695	0.322
40% C ₆ D ₆ :60% C ₃ D ₈ O ^b	3.097	3.272	4.668	3.557	5.020

^a Relative to TMS = 0.0 ppm. ^b Relative to benzene = 7.30 ppm; these values may differ by up to -0.6 ppm when compared to TMS.

H₆ is more shielded in the mixed solvent, thereby increasing the separation of H₄ and H₆.

The nuclear Overhauser effect experiment was run on II in C₆D₆ and found to be negative for H₉ when H₃ was irradiated. In structure II, H₉ and H₃ are located only about 1.2 Å apart and should exhibit an approximate 45% NOE area increase if H₉ is inside the cage. Since the effect was found to be negative, the proton must be outside the cage part of the molecule. Further evidence was provided by the ¹H-FT spectra of II (on 4.6 mg). Decoupling of H₂ made H₉ into a singlet, proving the exo to cage structure of H₉ of II ($J_{2,9} = +.32$ Hz which is a long range coupling). In addition H₃ became a doublet, H₄ became a triplet, and H₆ became a small doublet ($J = \sim 2$ Hz), thus proving all of the above relationships of H₂ and confirming the structure of II. The fact that H₉ is coupled to H₂ not only shows the outside cage relationship of H₉ but also shows that the bridge of II is located as shown. A detailed analysis of the nmr spectra will be published separately. This information plus that obtained by uv, mass spectrometry, and infrared spectroscopy shows the structure of II to be that shown in Figure 1. The orientation of the hydrogen and chlorine atoms at C₃ and C₅ for II has not previously been suggested or determined.

A possible mechanism is shown in Figure 10. The formation of II *vs.* III probably is a competitive one based on relative rates from a common intermediate. This may be a π -stabilized radical resulting from either the loss of a hydrogen radical or preferably by an intermolecular hydrogen abstraction that occurs from a nearby I molecule in the crystal. Path one shows the formation of structure II. Path two shows the formation of III, which probably is formed from those molecules that do not have a convenient I molecule nearby for radical hydrogen abstraction and so an intramolecular hydrogen transfers from C₃. H₉ in III is *cis* or *trans* to H₈, more likely *cis* from the coupling constant. Upon further ultraviolet irradiation, III proceeds through a π -stabilized diradical with the formation of structure IV. Path three, which results in the C₉ hydrogen being outside the cage, also appears to be possible but our work suggests that only II and III are formed initially, with IV appearing with the loss of III. Work is continuing to determine the absolute configuration of molecules III and IV.

The KBr solid state technique for study of molecular degradation is a useful tool which has been applied to the study of thermal (Graham and Kenner, 1969) and ultraviolet induced isomerizations. Most of the resulting products as characterized by their infrared spectra have been found to be the same as those derived in nature by heat or light. A study of consecutive infrared spectra collected on a time exposure basis helps to identify intermediates if present and their relative stability to the exposure conditions. Since all measurements are made on a captive sample in KBr, certain quantitative relationships as well as rate studies can be made. The technique is versatile in that decomposition can be controlled by time of exposure to produce a maximum amount of intermediate or final degradation product or products which can easily be re-

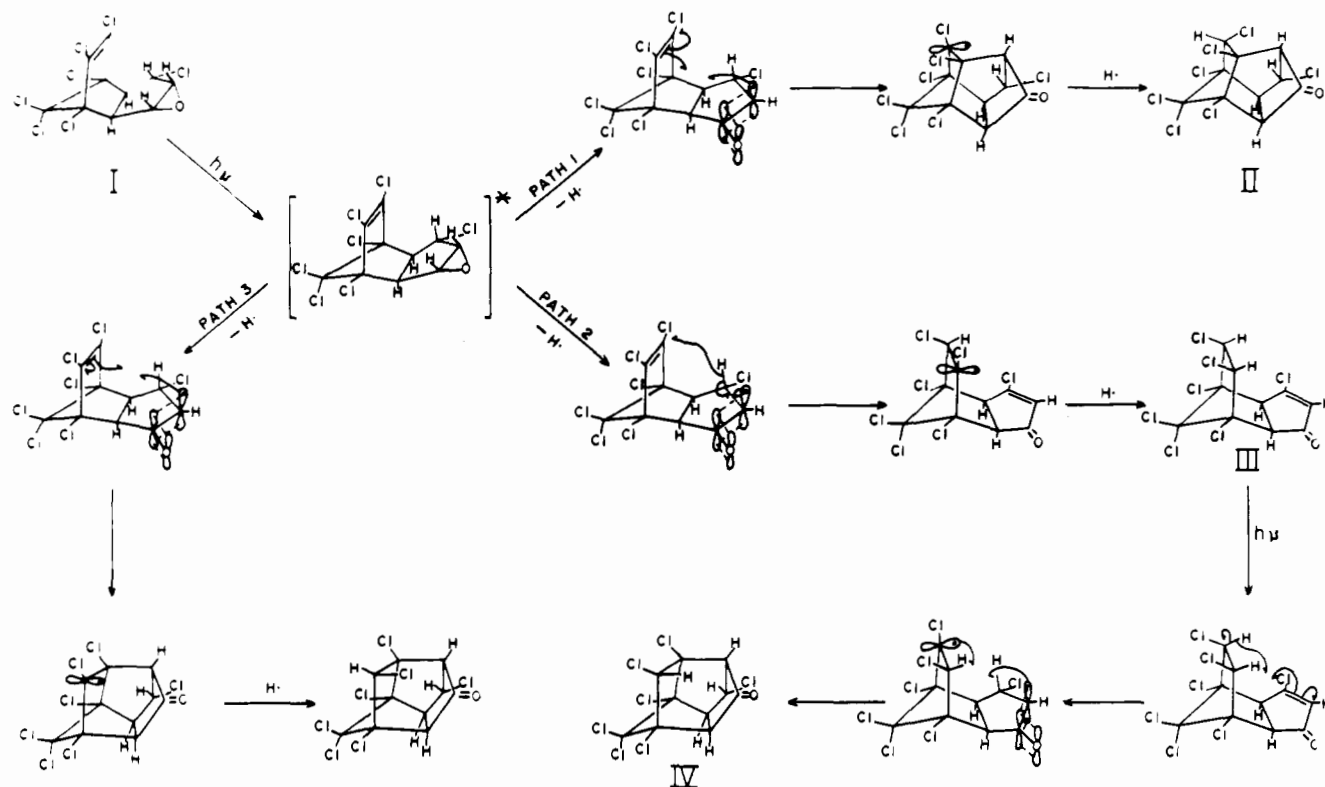


Figure 10. Tentative mechanism.

covered from the KBr disk for thin-layer chromatography, gas-liquid chromatography, infrared, ultraviolet, mass spectrometry, or nuclear magnetic resonance as desired.

The technique is presently being applied to the investigation of the decomposition of steroids in this laboratory.

ACKNOWLEDGMENT

We would like to acknowledge the kind assistance of Teijiro Yonezawa of Kyoto University of Japan for making his HR-220 nmr spectrometer and computer facilities available to one of us (C.F.H.) and to Makoto Takeuchi of JEOL Ltd., of Akashima, Japan, for his assistance in obtaining ^1H -FT spectra (coupled and decoupled) of II. We thank Kurt Loening of Chemical Abstracts Service, Columbus, Ohio, for the von Baeyer and Chemical Abstract names used in the manuscript.

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Received for review January 24, 1973. Accepted June 11, 1973.