THE PHOTOLYSIS OF HEPTACHLOR

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ABSTRACT

The Photolysis of Heptachlor

By

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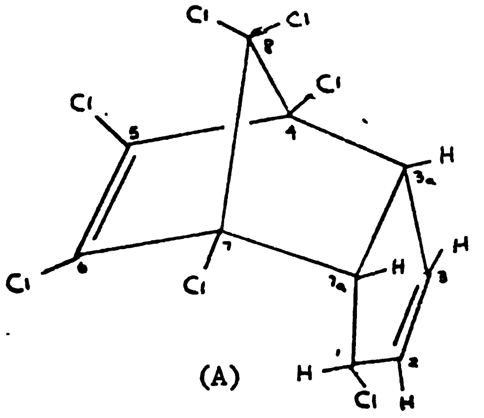
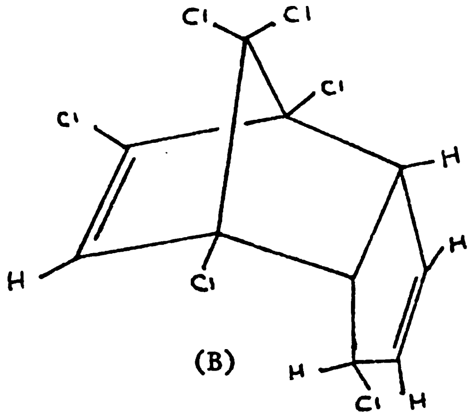
Heptachlor (A), a widely used polycyclic chlorinated hydrocarbon insecticide, one of a family of chlorinated insecticides derived from cyclopentadiene and hexachlorocyclopentadiene was found to give three major products on photolysis with ultraviolet light.

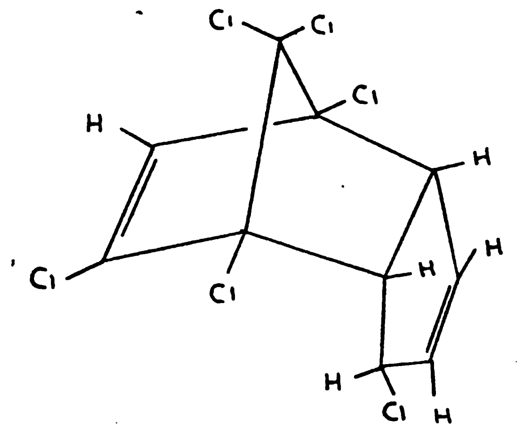


(A)



(B)

Photolysis in hexane, a protic solvent which is not triplet sensitizing, yields mainly two photodechlorination products, 1,4,5,7,8,8-hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (B) and 1,4,6,7,8,8-hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (C), and a small amount of the cage compound 2,3,4,4,5,6,10-heptachloro-pentacyclo$[5.3.0.0^{2,6}.0^{3,9}.0^{5,8}]$decane. The photodechlorination reaction very probably occurs via the excited singlet state.



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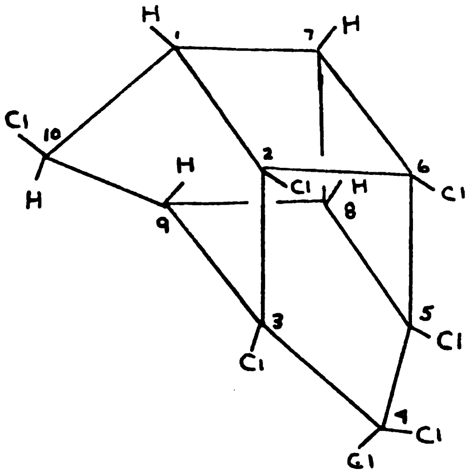

(D)

Photolysis in acetone, a protic solvent which is also triplet sensitizing, gives exclusively the cage compound formed by 4π cycloaddition. C. M. Anderson (1) described similar results using other polycyclic chlorinated hydrocarbons.

1. C. M. Anderson, J. B. Bremner, I. W. McCay, and R. W. Warrener, Tet. Letters, <u>10</u>, 1255 (1968).

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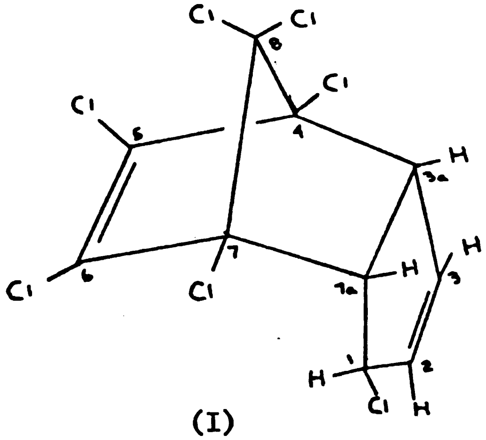
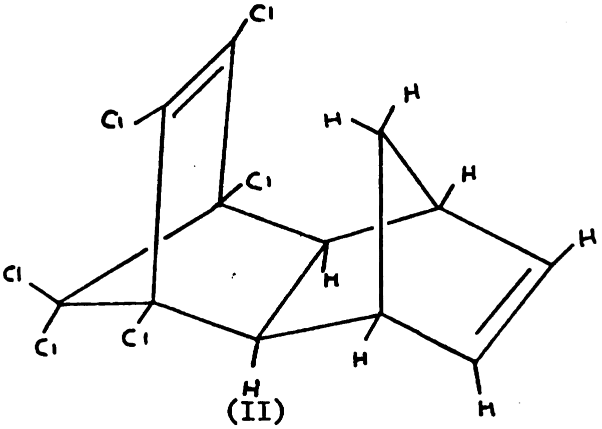
INTRODUCTION AND HISTORICAL

Heptachlor (I) is but one member of a series of highly chlorinated hydrocarbons produced by the Diels-Alder reaction of cyclopentadiene with hexachlorocyclopentadiene. Additional members of this series include aldrin (II), dieldrin (III), and chlordene (IV).



(I)



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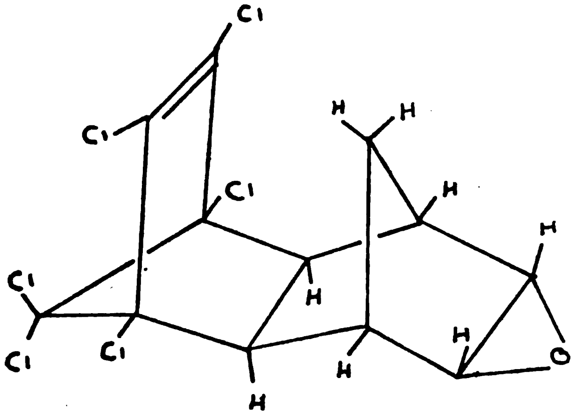

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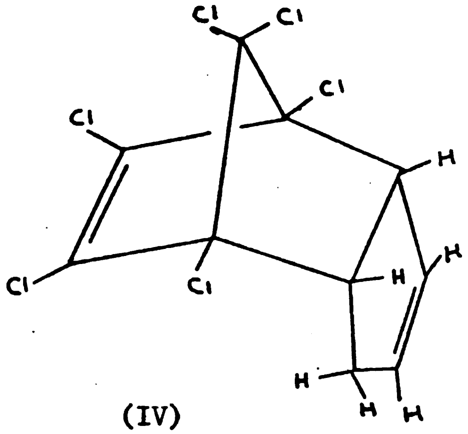


(IV)

The use of these polycyclic chlorinated compounds in the agricultural industry is widespread. Attempts are being made to replace them with the phosphate esters and phosphate thioesters which are more toxic to mammals but are much less stable, yielding harmless residues on hydrolysis. The strong possibility of the destruction of wildlife, both in the fields and waters by concentration of the chlorinated insecticides in animal bodies has been reported Sterility in predatory animals is also feared. The most favorable property for the commercial use of the chlorinated hydrocarbons is their low production cost, as they are readily produced from inexpensive starting materials and by simple reactions.

The persistence of these compounds depends upon the method of application, the soil type, and weather conditions. Heptachlor mixed in soil showed approximately 53% retention after 21 months (1), independent of whether the soil was dry sandy soil, loam, or swamp muck. Heptachlor adsorbed to the surface of the soil was found to be nearly eliminated in from 8-11 days; the pesticide being lost most quickly from moist soil exposed to sunlight. Heptachlor is easily hydrolyzed to its epoxide but otherwise is quite stable.

Heptachlor is a broad spectrum insecticide and finds a wide variety of uses. Its persistence especially suits it to uses in which repeated applications are to be avoided.

Toxicity studies have shown heptachlor to be moderately toxic to mammals. The L.D.$_{50}$ values vary somewhat but for rats are about 400mg of pesticide per kg of body weight. It is less toxic than aldrin, dieldrin, or malathion, an example of the phosphate thioesters.

Chlordene (IV) $C_{10}H_6Cl_6$, the precursor of heptachlor is formed by the Diels-Alder reaction of cyclopentadiene with hexachlorocyclopentadiene. The direct chlorination of chlordene in the dark results in the formation of heptachlor. A 1-3% concentration of Fullers earth or aluminum oxide is used as a catalyst. Heptachlor is sold as a 25%

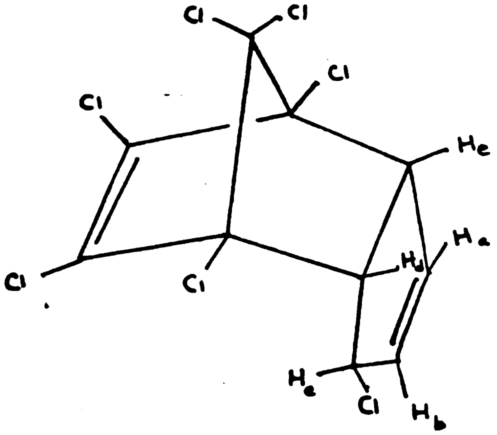
wetable powder on Fullers earth, or dissolved in toluene or kerosene

The photolysis of pesticides as a means of their destruction in the environment has been rather widely investigated. For this reason the study of the photolysis of heptachlor was undertaken. If the photolysis products identified in the laboratory are the same as those obtained from insecticide applied to plants in the field, a link between photolytic decomposition of heptachlor in the environment and that induced in the laboratory could be obtained. This would allow detailed study of the rates of photolysis of the pesticide, its photolytic products, and determination of their toxicity to mammals and particularly to man.

RESULTS AND DISCUSSION

Heptachlor undergoes a facile photolysis. Photolysis of a 200ml. volume of a 1.5% solution of heptachlor in hexane results in the formation of two major photoproducts amounting to approximately 85% of the total mixture. Reaction of heptachlor with a 200W. Hanovia high pressure mercury lamp without filters and through quartz requires 130-150 minutes for complete photolytic conversion of the above solution. A gradual decrease in the concentration of heptachlor in the reaction mixture is observed in samples removed periodically during the photolysis and subjected to gas chromatographic analysis. With longer reaction times or higher concentrations of heptachlor, secondary reactions are observed including considerable formation of polymer from hexane. The evolution of HCl gas is noted during both primary and secondary reactions. Since a comparison between the photolysis products formed in the laboratory and those formed under field conditions was desired, and since the separation of multiple products becomes infinitely more difficult, photolysis was restricted to the shortest reaction periods consistant with the total conversion of heptachlor.

Heptachlor, 1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene, is a white crystalline solid melting in the range 92-95°C. It sublimes readily in vacuo at 60°C. It decomposes if heated much above its melting point. It gives a distinctive nuclear magnetic resonance spectrum, not entirely consistent with what would be expected from analysis of models of the compound. A quartet appears at 6.5τ, an octet at 5.9τ, and a multiplet at 5.2τ, in the ratio 1:1:1. A two proton singlet appears at 4.1τ. The quartet at 6.5τ is assigned to H_d, a proton which is neither allylic or vinyl. The octet at 5.9τ is assigned to H_e. H_e is an allylic proton split by H_a, H_d, and the long range splitting of H_b. The multiplet at 5.2τ arises from H_c. H_c is an allylic proton but is shifted further downfield than H_e by the geminal chlorine. The two proton singlet at 4.1τ arises from H_a and H_b. This is consistent with the olefinic protons on norbornene which fall at 4.06τ. It is only by chance that H_a and H_b give a singlet. There is no plane of symmetry in the molecule. The angles between H_a and H_e or H_b and H_c are both 75°, in which case splitting is expected.



The infrared spectrum of heptachlor is quite complex, owing to the presence of a large number of chlorine atoms in the molecule. A sharp characteristic olefinic stretching frequency is evidenced by a medium a absorption at 3090 and 705 cm^{-1}. A broad absorption at 2920 cm^{-1} arises from the aliphatic C-H stretching frequency. Due to their complexity, analysis of the C-Cl absorptions which are many and which fall within the 600-800 $cm.^{-1}$ range is not possible. A mass spectrum of heptachlor was obtained to determine the type of fragments which could be expected from a molecule of this type. Peaks were obtained which correspond to m/e 369, 334, and 298, for the ion fragments $C_{10}H_4Cl_7$, $C_{10}H_5Cl_6$, and $C_{10}H_3Cl_5$.

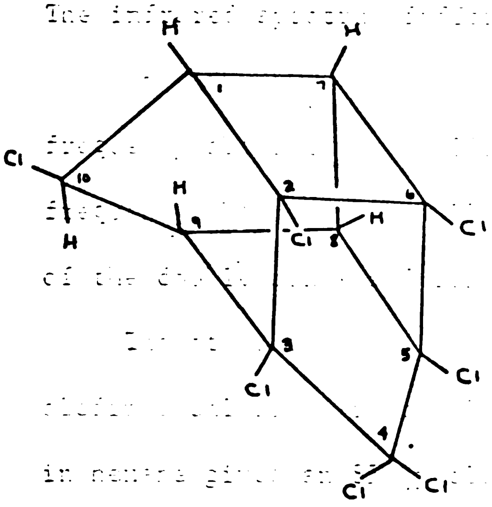
Two competing reactions occur when heptachlor is photolyzed in hexane, both of which were previously known for similar model compounds. The intermolecular 4π cycloaddition reaction, closure of two double bonds to form a cyclobutane ring, giving a birdcage compound related to the cubane system has been noted in many cases. The Woodward-Hoffman rules (2) predict this to be an allowed photochemical process. Examples of compounds which are known to undergo reactions of this type are 3a,4,7,7a-tetrahydro-4,7-methanoindene (the dicyclopentadiene dimer) (3) and aldrin (II) 1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4-endo, endo-5,8- dimethanonaphthalene (4). The cage compound 2,3,4,4,5,6,10-heptachloropentacyclo $[5.3.0.0^{2,6}.0^{3,9}.0^{5,8}]$decane (V) is obtained in 5% yield from the photolysis of heptachlor in hexane. Photolysis of heptachlor in acetone yields the cage compound (V) as the exclusive product. Initially, the cage compound was obtained by column chromatography from the photolysis mixture in hexane. It was later obtained in larger quantities by vacuum sublimation of the residue from photolysis in acetone. Final purification in both cases was injection through a 6' X 1/8", 5% DC 11 on 60/80 mesh Gas-Chrom Q column in the gas chromatograph. Fraction collection gave a white crystalline compound melting in the range 118-119 . Analysis of the infrared spectrum showed both compounds to be the same.

The cage compound gives a nuclear magnetic resonance spectrum with only two absorptions, a multiplet (4H) at 6.6τ and a multiplet (1H) at 5.45τ. The latter absorption arises from the proton geminal to a chlorine. The other four protons are non-identical but have similar environments. The mass spectrum shows peaks corresponding to m/e 369,335, and 298, for ion fragments $C_{10}H_4Cl_7$, $C_{10}H_5Cl_6$, and $C_{10}H_3Cl_5$. The absence of ion fragments above 369 proves that the compound is not a dimer of heptachlor formed by intramolecular 4π cycloaddition. The infrared spectrum differs from that of heptachlor and the two other photoproducts in the absence of the olefinic stretching frequency absorptions at 3090 and 705cm.$^{-1}$, and the olefinic stretching frequency absorptions at 1580cm.$^{-1}$. This is consistent with the loss of the double bonds and ring closure.

The other two products result from photodechlorination of the olefinic chlorines in the 5 or 6 positions of heptachlor. Photolysis in hexane gives an 85% yield of these two products. In acetone no photodechlorination products are obtained. Due to the asymmetry of the molecule resulting from the chlorine in the 1 position, the two photoproducts are not identical but posses very similar properties. The close similarity led to considerable difficulty in the separation and purification processes of these materials. Separation was laboriously brought about by using the gas chromatograph. Separate, consecutive injections and passages through two columns were used. Samples were separated into two fractions by passing them through a 4' X 1/8" column packed with 5% carbowax 20 M on 60/80 mesh Gas-Chrom

Q. Attempts at separation using thin layer or column chromatography were unsuccessful.

Structural assignments for the photodechlorination products, 1,4,5,7,8,8-hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (VI) and 1,4,6,7,8,8-hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (VII), are based on the NMR, infrared, and mass spectral data determined for these compounds. It is not possible to determine which structure belongs to which isomer. They are referred to here in terms of the order of elution from the carbowax gas chromatography column.



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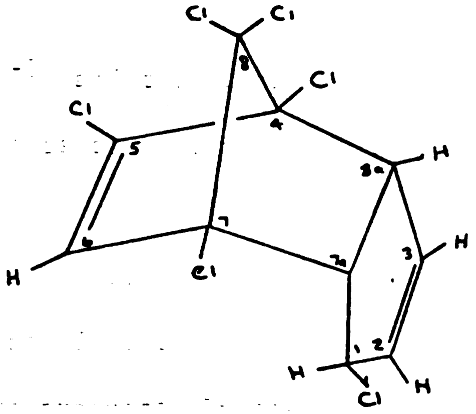
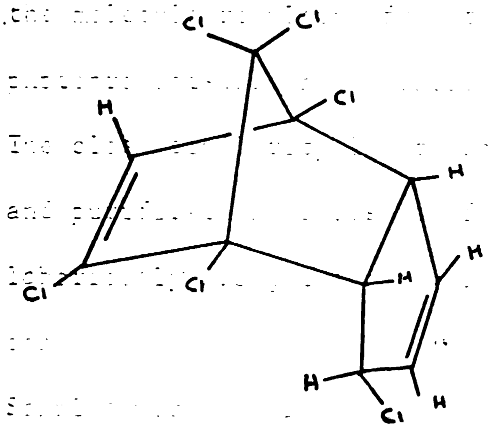
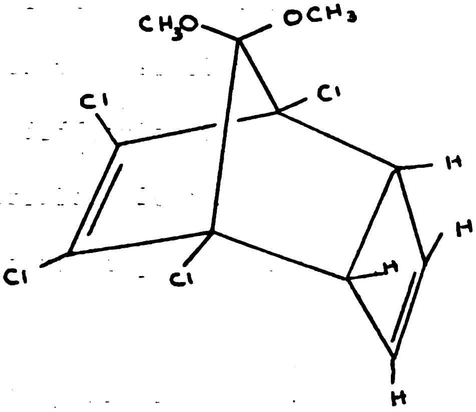


(VI)



(VII)



(VIII)

The nuclear magnetic resonance spectra for the two photodechlorination compounds are similar to that of heptachlor with the exception of an extra singlet (1H) and slight shifts in the field positions of all groups. For the first photoproduct, multiplets are found at 6.50,6.07, and 5.42τ. In heptachlor these correspond to H_d, H_e, and H_c respectively. A singlet (2H) is observed at 4.25τ, and a singlet (1H) is observed at 4.20τ. The latter reflects the proton added due to photodechlorination. This singlet is shifted somewhat downfield from the singlet (2H) at 4.25τ and falls mostly under the base of the larger singlet absorption. A peak at 4.1τ is due to a small amount of heptachlor in the sample. For the second photodechlorination product, peaks were obtained at 6.52 (1H), 6.09 (1H), 5.50 (1H), 4.30 (2H), and 4.20τ (1H).

The infrared spectra for the photodechlorination products are nearly identical except for slight differences in the intensities of some peaks. The intensity of the vinyl proton C-H stretching frequency absorption is greater than that of heptachlor, reflecting the influence of the added proton. The absorptions due to unsaturation and mentioned for heptachlor are all present in the spectra of the two photodechlorination compounds. Since the total change in the structure is small, little change in the infrared spectrum is expected.

The mass spectra of the two photodechlorination products were essentially the same. Peaks were obtained for m/e 335, 300, and 264 for ionic fragments $C_{10}H_5Cl_6$, $C_{10}H_5Cl_5$, and $C_{10}H_4Cl_4$ respectively. No evidence of any fragment is the m/e 369-379 region or above was found. This rules out the formation of a dimer.

An attempt was made to influence the ratio of the reaction products in the manner described by C. M. Anderson et. al. (5). Anderson has shown that photodechlorination probably occurs via the excited singlet state while the 4π cycloaddition reaction occurs via the excited triplet state. Photolysis of the tetrachloroketal (VIII) in acetone using a vycor filter gave only the bird cage compound. Acetone acts here as a triplet sensitizer, although it may also be a source of abstracted protons. Reaction of the tetrachloroketal (VIII) in ether by using a pyrex filter gave photodechlorination of the olefinic chlorines. However, there were complicating secondary reactions. In a similar manner the reaction of heptachlor gave only the cage compound when photolyzed in acetone (no filter) and mainly the photodechlorination compound in hexane, a solvent which is a source of hydrogen but not a triplet sensitizer.

In order to rule out a change in the carbon skeleton for the photodechlorination compounds, a reductive dechlorination was carried out on the total photolysis mixture. The solvent was removed from the photolysis mixture and the remainder was distilled in a molecular still to remove polymer formed by the photolysis of the solvent. A dissolving metal reduction was carried out by using lithium and tertiary butyl alcohol. Gas chromatographic analysis of the recovered dechlorinated compound showed it to be 65% dicyclopentadiene. Infrared analysis of samples collected from the gas chromatograph showed this 65% portion to be identical with a commercial sample of dicyclopentadiene. Thus changes in the carbon skeleton were ruled out for photodechlorination.

EXPERIMENTAL

All melting points were determined on an Electrothermal melting point apparatus and are uncorrected. Infrared spectra were determined with a Perkin-Elmer 337 grating spectrophotometer either neat on sodium chloride plates or as potassium iodide pellets. All ultraviolet spectra were determined in 95% ethanol using a Unicam SP 800 or a Beckman DB-G spectrophotometer. Nmr spectra were obtained using a Varian A-60 nuclear magnetic resonance spectrometer. Gas chromatographic analyses were obtained from a Beckman GC-4 equipped with a fraction collector and employing either a hydrogen flame or a thermal conductivity detector. Mass spectra were obtained from an LKB gas chromatograph-mass spectrometer. Elemental analyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Michigan.

Purification of Heptachlor

Heptachlor was obtained as a 25% wettable powder or as a 25% solution in toluene or kerosene. Heptachlor was extracted from the diatomaceous earth used as an absorbant in the wettable powder form by using acetone or ether as an extracting solvent. The extracting solvent was removed and the crystalline solid was redissolved in hot ethanol. The ethanol solution was decolorized with activated charcoal. Successive recrystallization of the crystals thus obtained gave heptachlor with a purity greater than 99% as indicated by gas chromatographic analysis. For heptachlor in a toluene or kerosene solution a procedure similar to the above was followed after crystalline material had been obtained from the original solutions through evaporation of the toluene or kerosene. The wettable powder formulation is available from Stauffer Chemical Company and the solution formulations from Vesicol Chemical Company.

Photolysis of Heptachlor in Hexane

Photolysis reactions were carried out by using a 200 W Hanovia high pressure mercury lamp in a 250 ml capacity pyrex reactor vessel fitted with a water cooled quartz core. The bottom of the vessel was flattened to allow for a magnetic stirrer and was fitted with a stopcock to permit nitrogen to be bubbled through the reaction mixture. In a typical reaction 3 g of heptachlor was dissolved in 250 ml of hexane and the reaction solution was placed in the reaction vessel. Nitrogen was slowly bubbled through the solution and stirring was provided by using a magnetic stirrer. During photolysis, samples were periodically removed from the reaction vessel and analyzed gas chromatographically. Photolysis reaction periods of 130 - 150 minutes were required for complete conversion of the heptachlor to its photolytic products in the above solution.

Noticeable quantities of hydrogen chloride gas were evolved during the photolysis reaction. A gradual darkening of the solution occurs during the course of the reaction. Photolysis of hexane alone produces the same color change but requires longer periods of photolysis. Removal of the hexane from the heptachlor reaction solution leaves a light brown viscous liquid. Hexane apparently undergoes a photolytic free radical reaction to form a brown polymeric material.

Photolysis of Heptachlor in Acetone

Photolysis of heptachlor in acetone was carried out by using the same procedure and equipment as that for the photolysis of heptachlor in hexane, excepting that a 350 ml reactor vessel was used. A 1 g sample of heptachlor was dissolved in 350 ml of acetone and photolyzed for 7 hours. At the end of this time period gas chromatographic analysis of the reaction mixture by using a 6' X 1/8", 5% DC 11 on Gas-Chrom Q column showed only a single product and a small amount of unreacted heptachlor. Removal of the acetone resulted in the formation of a crystalline material on the walls of the flask. Vacuum sublimation of these crystals followed by purification by using a 5% DC 11 column at 140°gave crystals which were found to be identical to the cage compound obtained from the photolysis of heptachlor in hexane.

Purification of the Cage Compound

Isolation of the cage compound was first achieved by using column chromatography in an unsuccessful attempt to separate the two photodechlorination compounds. A column, 3/4" in diameter, was filled to a depth of 8" with an alumina-hexane slurry. Activity I chromatographic grade alumina was used. A 1 g sample of the photolysis mixture was placed on the column by using a medicine dropper. Passage of the photolysis mixture into the column was followed by 100 ml of hexane. Next 100 ml of 1% $CHCl_3$ in hexane and then 100 ml of 5% $CHCl_3$ in hexane were passed through the column. Samples, 10 ml in volume, were collected from the eluted solvents. The photodechlorination products were found in fractions 5 to 17. The cage compound was obtained as a crystalline material in fractions 25 to 35. The crystalline material was redissolved in acetone and chromatographed at 140° on a 6' X 1/8", 5% DC 11 on 60/80 mesh Gas-Chrom Q column. A pure white needlelike crystalline material was obtained from the fraction collector. It melted in the range 118-119°. The nmr spectrum gave a multiplet at 5.45τ (1H) and a multiplet at 6.6τ (4H). No infrared absorptions can be attributed to C=C stretching frequencies (1580 cm^{-1}) or to =C-H stretching frequencies (3090 and 705 cm^{-1}). The mass spectral determination of the cage compound gave peaks m/e 369, 335, and 298. No indication of higher masses was evident, ruling out the formation of a dimeric product.

Analysis: Calculated for $C_{10}H_5Cl_6$: C, 32.17; H, 1.35; Cl, 66.47
Found: C, 32.42; H, 1.42; Cl, 66.16.

Purification of the Photodechlorination Compounds

Samples were purified by first injecting the mixture into a 4' X 1/8" 5% Carbowax 20M on 60/80 mesh Gas-Chrom Q column at 180° and collecting the two fractions using the fraction collector. Samples were further purified by injection into a 6' X 1/8", 5% DC 11 on 60/80 mesh Gas-Chrom Q column at 160°.

Since the photoproducts differ only by the interchange of protons and chlorines in the 5 and 6 positions, it was not possible to assign a definite structure to either of the compounds. They are referred to here as peak I and peak II, the order of their elution from the carbowax column.

Peak I

The compound from peak I is a white crystalline solid which only slowly crystallizes from the liquid obtained from the fraction collector. The infrared spectrum is in agreement with the structure proposed, having the same general features as heptachlor itself. In contrast to the cage compound, absorptions are present at 1580 cm^{-1} (C=C stretch) and 3090 and 705 cm^{-1} (=C-H). Additional proof of the presence of a double bond is the decolorization of dilute $KMnO_4$ and Br_2 in CCl_4. The nmr spectrum of I shows 6 protons, multiplets at 6.50 (1H), 6.07 (1H), 5.42τ (1H), and singlets at 4.25 (2H), and 4.20τ (1H). The singlet at 4.20τ which falls partially under the larger singlet at 4.25τ, corresponds to the proton substituted in the photodechlorination. It is shifted downfield by two viscinal chlorine atoms.

Analysis: Calculated for $C_{10}H_6Cl_6$: C, 35.44; H, 1.79; Cl, 62.77.
Found C, 35.17; H, 1.85; Cl by difference 62.98.

Peak II

The second photodechlorination compound has properties similar to those of the first photodechlorination compound. It is a white crystalline solid melting at 51-52°. The nmr spectrum for compound II is similar to that obtained for compound I except for slight changes in the field positions. Three multiplets appear centered at 5.5 (1H), 6.09 (1H), and 6.5τ (1H). Singlets are found at 4.30 (2H) and 4.20τ (1H). The infrared spectrum of II is identical to that obtained from I except for slight changes in the intensity of several of the absorptions. The mass spectra of the compounds gave peaks m/e 335, 298, and 264. No indication of any fragments corresponding to heptachlor or to a dimer was found.

Analysis: Calculated for $C_{10}H_6Cl_6$: C, 35.44; H, 1.79; Cl, 62.77.

Found: C, 35.61; H, 1.90; Cl, 62.64.

Dechlorination by Metal Reduction

A 100 ml, 3 neck, round bottom flask was fitted with a 50 ml dropping funnel, gas inlet valve, and a reflux condenser with drying tube. A magnetic stirring bar was placed in the flask. A 3 g quantity of lithium metal chips and 25 ml of tetrahydrofuran were placed in the flask and nitrogen gas was passed through the flask. A solution of 10 g of tertiary butyl alcohol, 25 ml of tetrahydrofuran, and 2.7 (~.008 m) of purified photolysis mixture was slowly introduced into the reaction flask. An exothermic reaction began after 10 minutes. The flask was cooled by immersion in an ice bath to keep the rate of reaction under control. After 15 minutes the reaction subsided and the mixture was allowed to reflux gently for 30 minutes without external heating. Heat was then applied by using a heating mantle. Gentle refluxing was continued for 1.5 hours to maintain refluxing. The heat source was removed, the mixture cooled, and the excess lithium chips were removed. The mixture was poured over cracked ice. The ice was removed and the aqueous solution was extracted with two 25 ml portions of ether. The combined etherial extracts were dried over $MgSO_4$ and the solvent removed under vacuum to yield 0.2 g of residue. Gas chromatographic analysis showed this to be 65% dicyclopentadiene. Fraction collection gave a sample with an infrared spectrum identical to that of commercial dicyclopentadiene. Thus skeletal rearrangements were ruled out.

SUMMARY

Photolysis of heptachlor in ultraviolet light produced three products. In the absence of a triplet sensitizer and using a protonic solvent, photodechlorination of the vinyl chlorines in the 5 or 6 position was observed. The photodechlorination products were identified as 1,4,5,7,8,8-hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (VI) and 1,4,6,7,8,8-hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (VII). Small amounts of the cage compound 2,3,4,4,5,6,10-heptachloropentacyclo-$[5.3.0.0^{2,6}.0^{3,9}.0^{5,8}]$decane (V), formed by 4πcycloaddition, was also obtained. In the presence of a triplet sensitizing protonic solvent only the cage compound (V) was formed. No evidence of dimer formation or changes in the carbon chain was found.

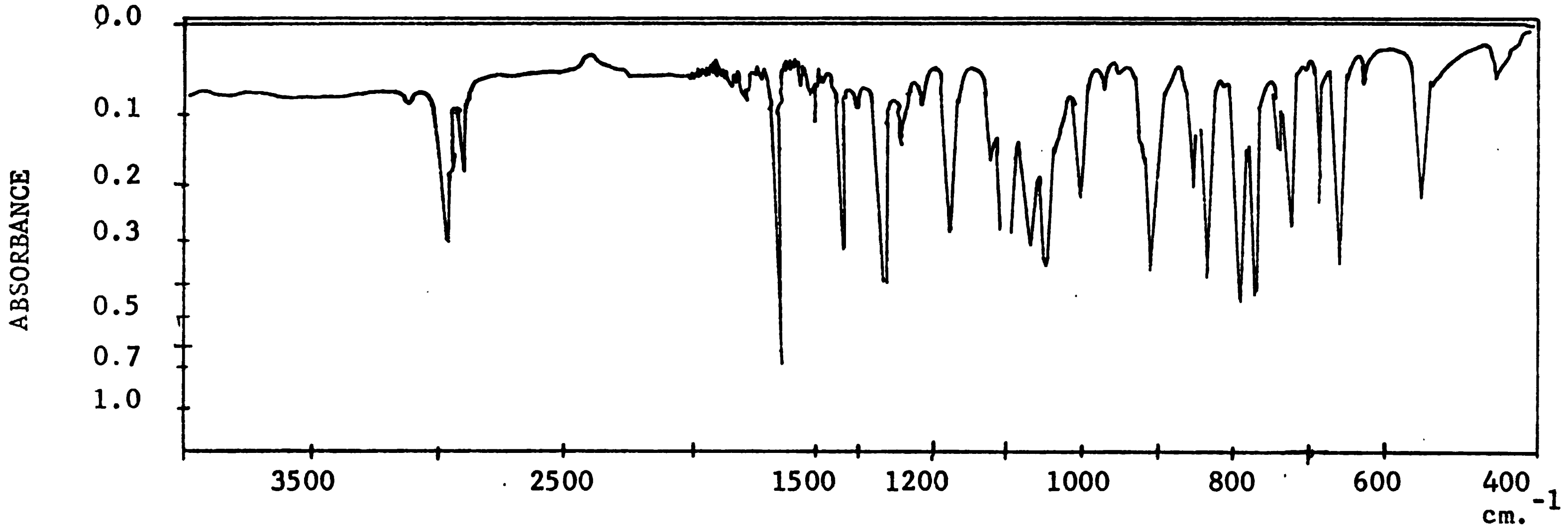


Figure 1. The Infrared Spectrum of Heptachlor

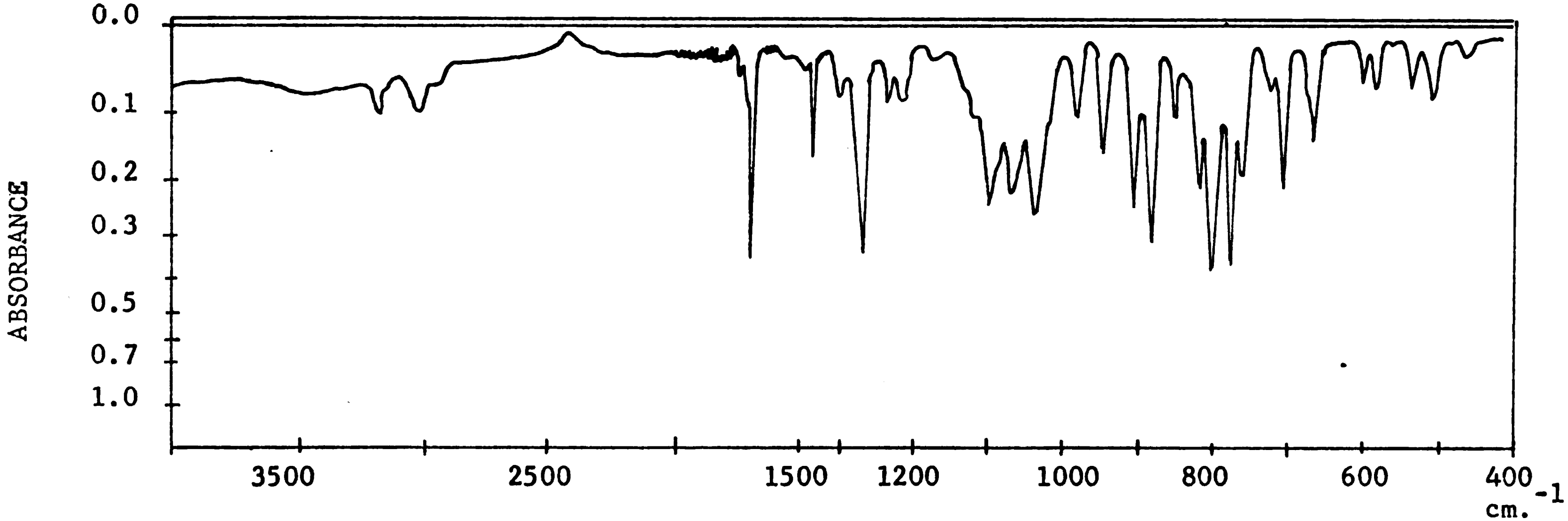


Figure 2. THE Infrared Spectrum of the First Photodechlorination Product.

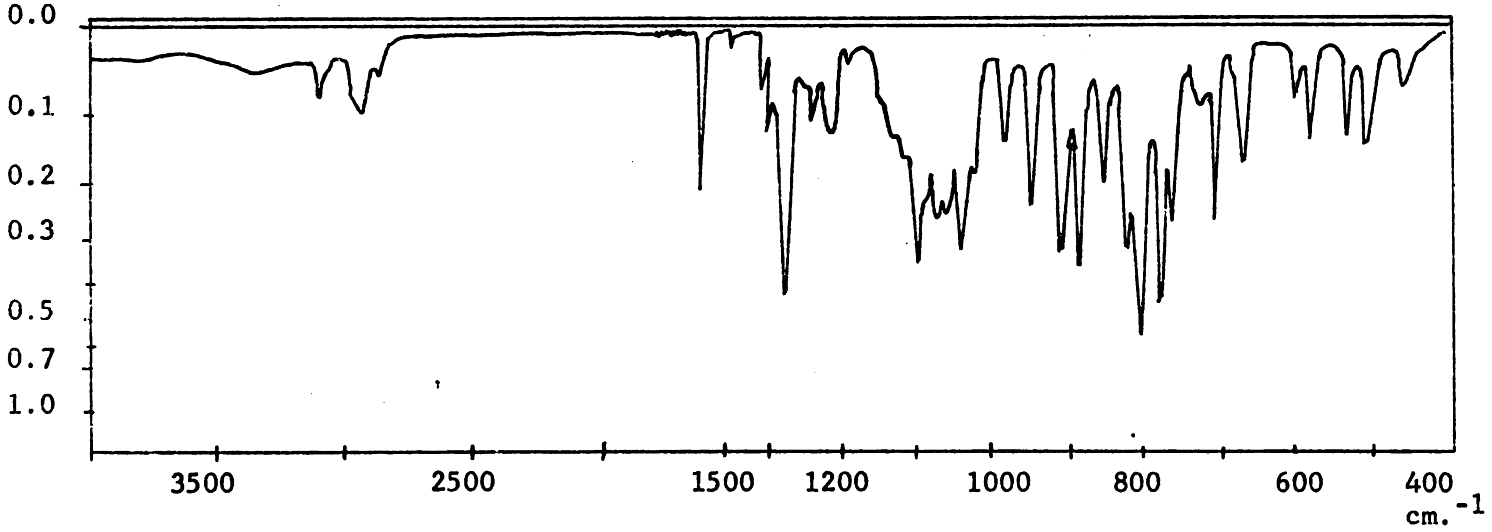


Figure 3. The Infrared Spectrum of the Second Photodechlorination Compound.

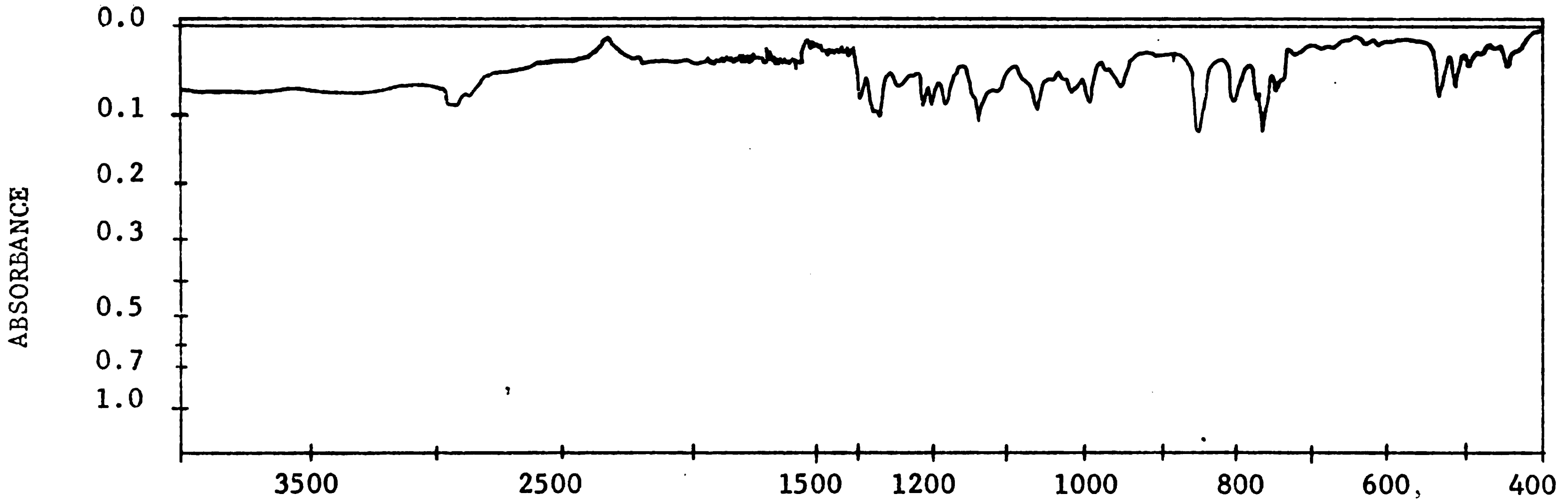


Figure 4. The Infrared Spectrum of 2,3,4,4,5,6,10-heptachloropentacyclo$[5.3.0.0^{2,6}.0^{3,9}.0^{5,8}]$decane.

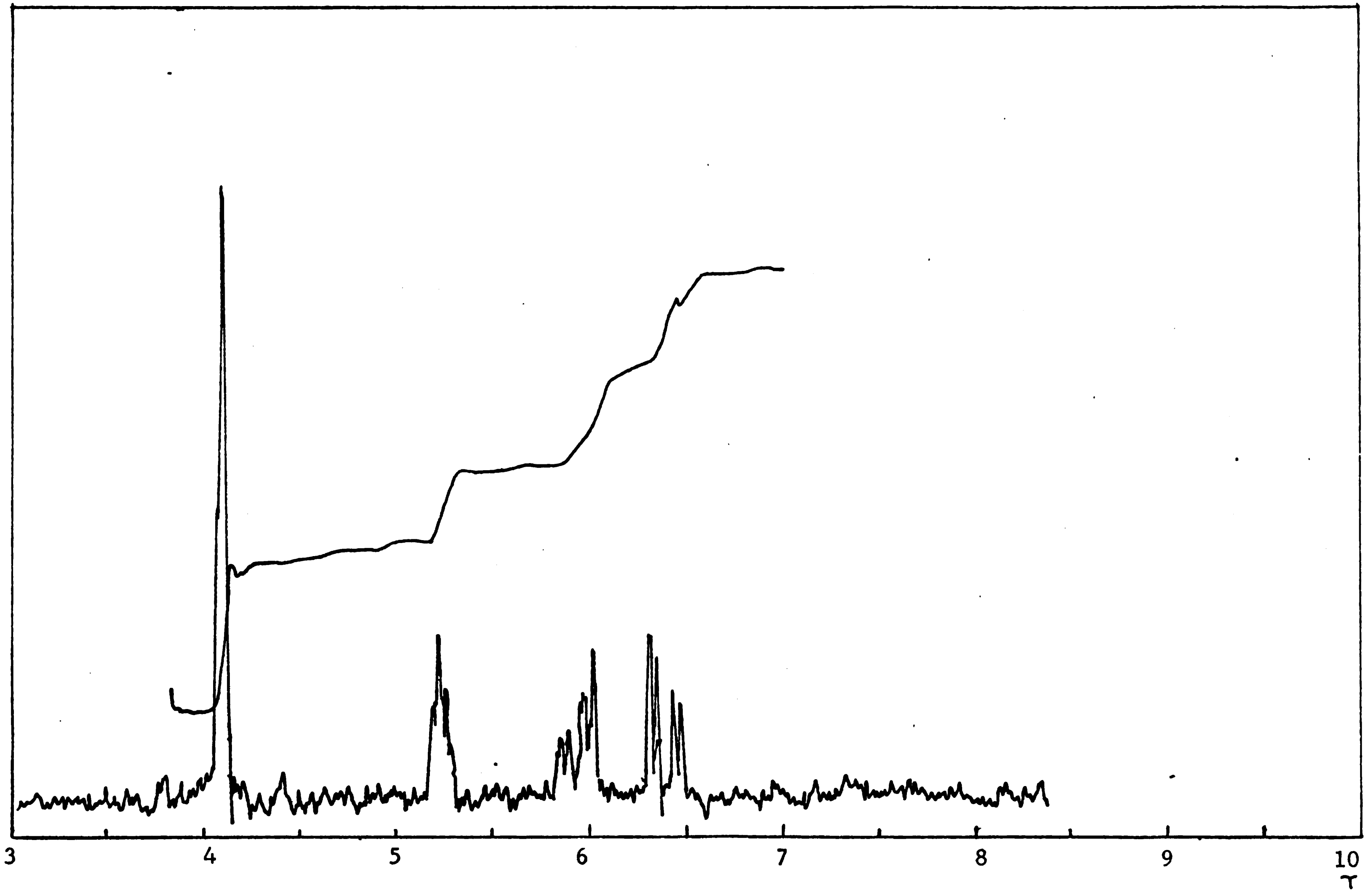


Figure 5. The NMR Spectrum of Heptachlor in CCl_4.

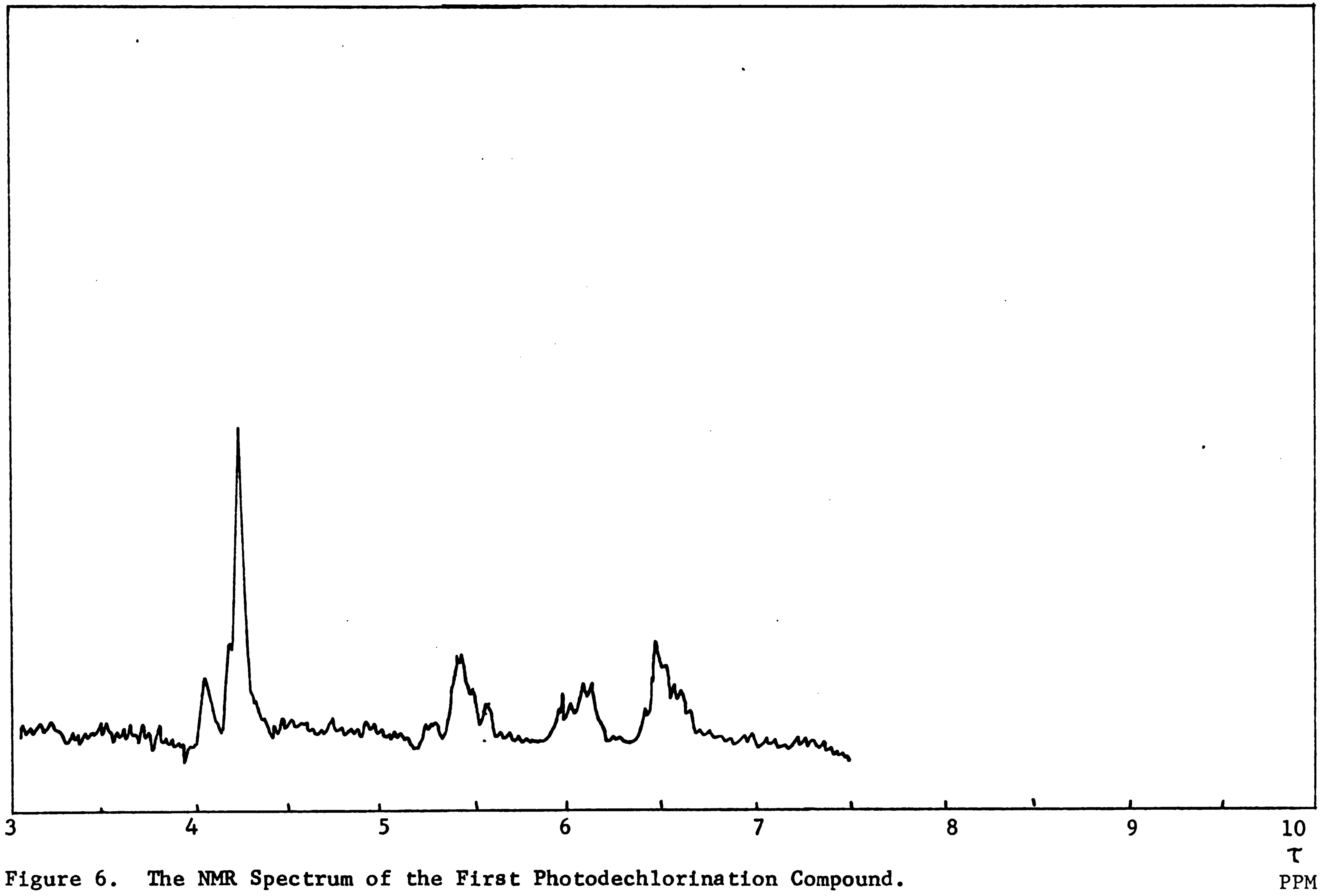


Figure 6. The NMR Spectrum of the First Photodechlorination Compound.

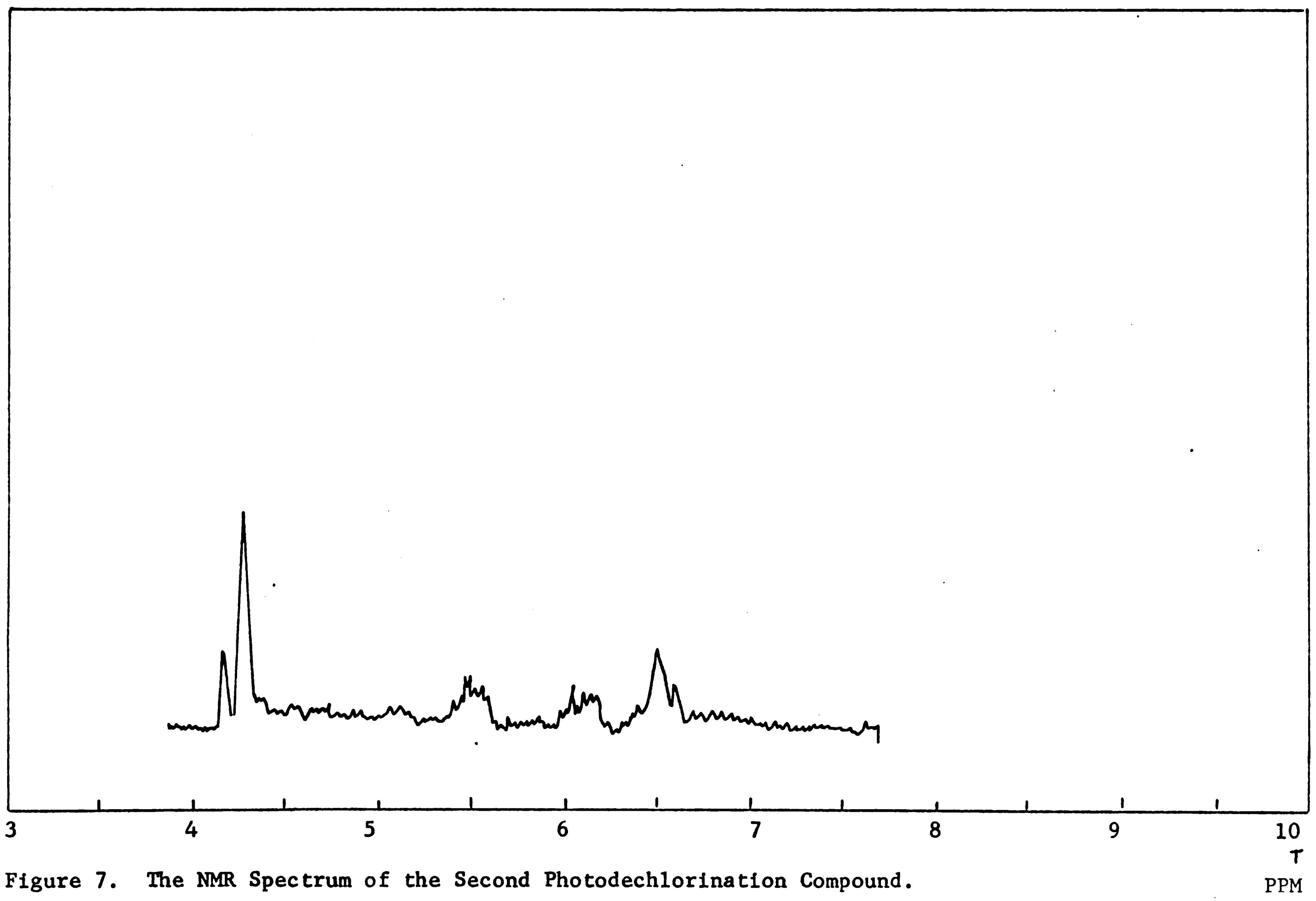


Figure 7. The NMR Spectrum of the Second Photodechlorination Compound.

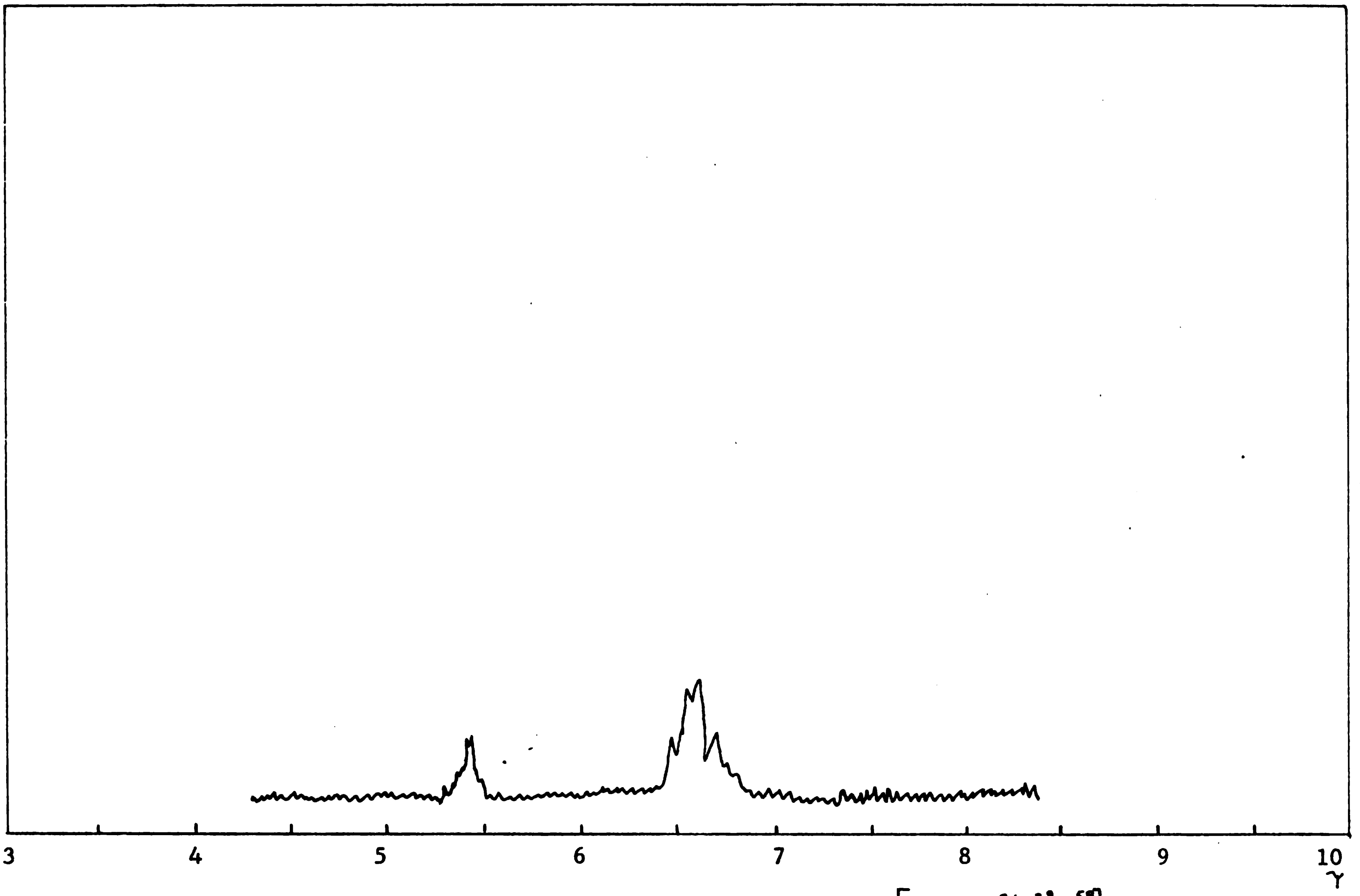


Figure 8. The NMR Spectrum of 2,3,4,4,5,6,10-heptachloropentacyclo$[5.3.0.0^{2,6}.0^{3,9}.0^{5,8}]$decane in CCl_4.

Table I. The Intensity of Isomer Peaks Compared to Parent Peaks in the Mass Spectrum.

Parent Peak and Source	Fragment Ion	P		P+2		P+4		P+6		P+8	
		F	E(6)	F	E	F	E	F	E	F	E
Cage Compound											
369	$C_{10}H_4Cl_7^+$	.152	.139	.311	.316	.319	.310	.165	.163		
335	$C_{10}H_5Cl_6^+$	.190	.184	.354	.360	.288	.293	.133	.128		
298	$C_{10}H_3Cl_5^+$	.244	.244	.392	.398	.264	.398	.088	.085		
Photodechlorination Compound I											
335	$C_{10}H_5Cl_6^+$	.187	.184	.348	.355	.278	.293	.158	.128	.029	.031
300	$C_{10}H_5Cl_5^+$	.263	.244	.379	.398	.268	.260	.089	.085		
264	$C_{10}H_4Cl_4^+$	.310	.323	.418	.422	.215	.206	.079	.044	.022	.004
Photodechlorination Compound II											
335	$C_{10}H_5Cl_6^+$	.197	.184	.368	.355	.276	.293	.132	.128	.026	.031
300	$C_{10}H_5Cl_5^+$	.262	.244	.410	.398	.262	.260	.066	.085		
264	$C_{10}H_4Cl_4^+$	.326	.323	.412	.422	.203	.206	.052	.044	.006	.004

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