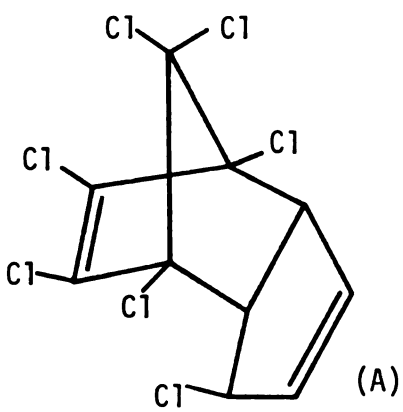
ABSTRACT

A MODEL SYSTEM: THE PHOTOCHEMICAL INTERACTION OF HEPTACHLOR AND SELECTED EPICUTICULAR WAX COMPONENTS OF THE TOMATO FRUIT AND PEAR LEAF

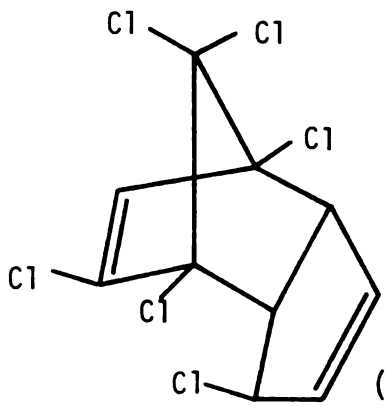
By

Janise Ehmann

Heptachlor (A), a cyclodiene insecticide was found to yield two hexachlor isomers, 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), at 310 nm under a variety of experimental conditions.

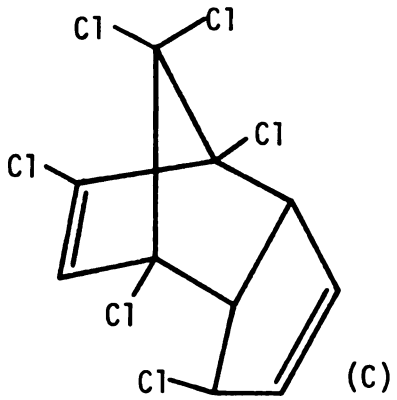


(A)



(B)

The structural isomer of Heptachlor, 2,3,4,5,6,10-heptachloro-pentacyclo [5,3,0,$0^{2,6,}$,$0^{3,9}$,$0^{5,8,}$] decane (D) was formed in relatively small amounts when Heptachlor film was exposed to the sunlight during the summer months.



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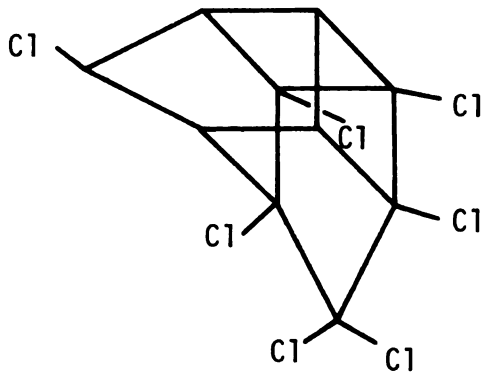
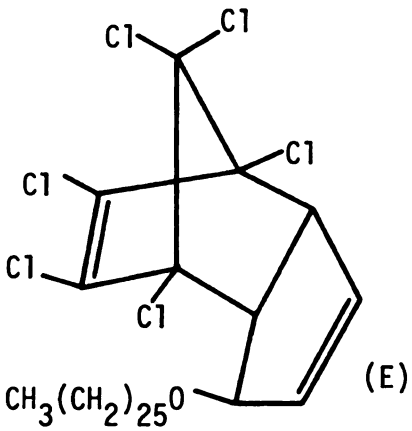


(D)

Photolysis of heptachlor in the presence of Ceryl Alcohol and acetone resulted in the photo-addition of the alcohol to the hexachlor either as an ether (E and F) or as a C-C linkage (G and H).



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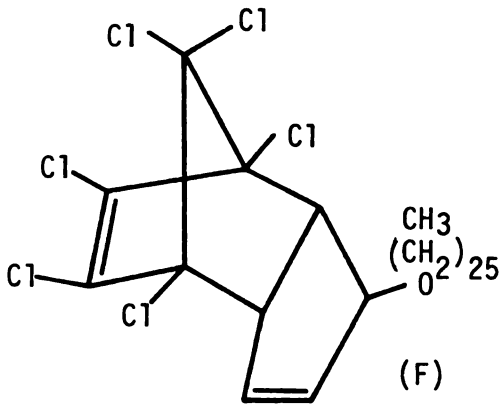

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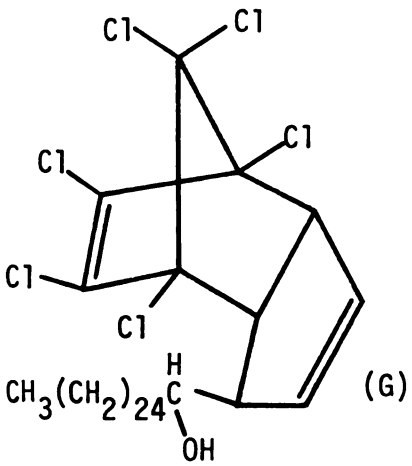

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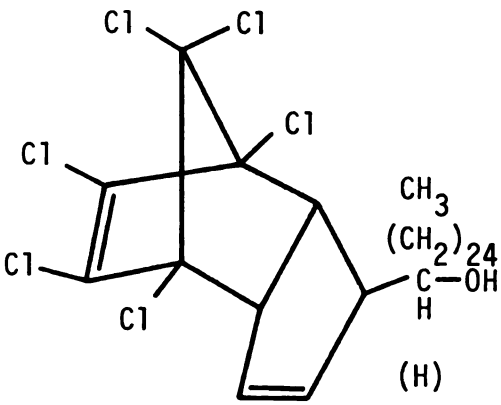
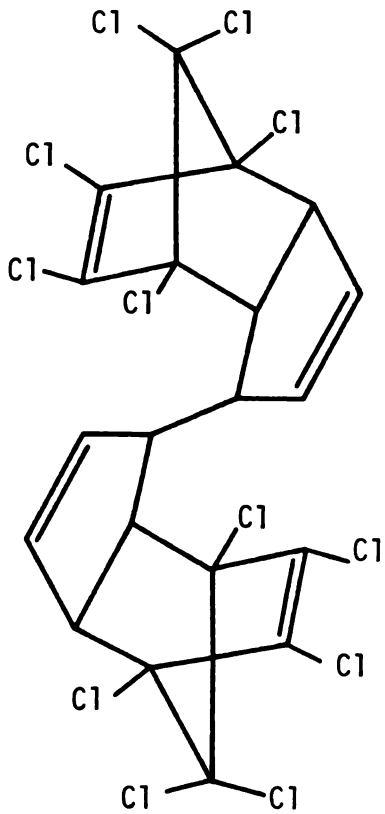
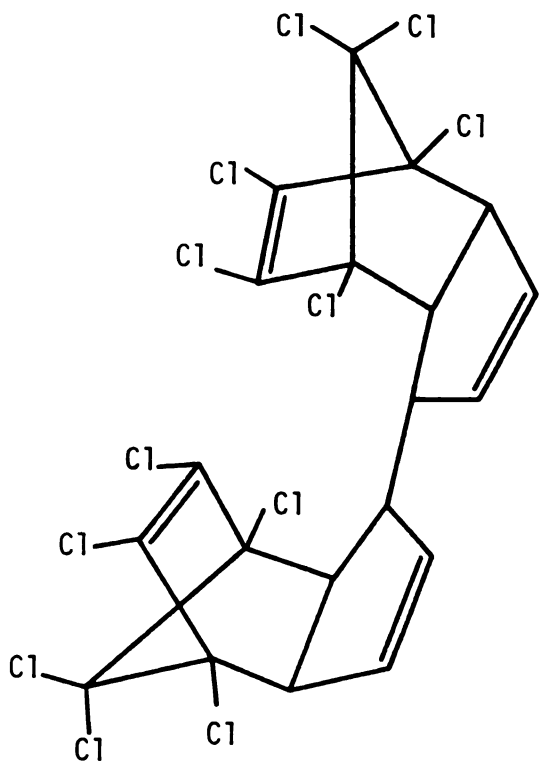


(H)

Photolysis of heptachlor under various experimental conditions, both in solution and as films produced several hexachlor dimers. The stereochemistry of the dimers and their isomers has only been suggested since these compounds were formed in relatively small amounts not sufficient to isolate and characterize further, at this time (I, J, K and L).



(I)



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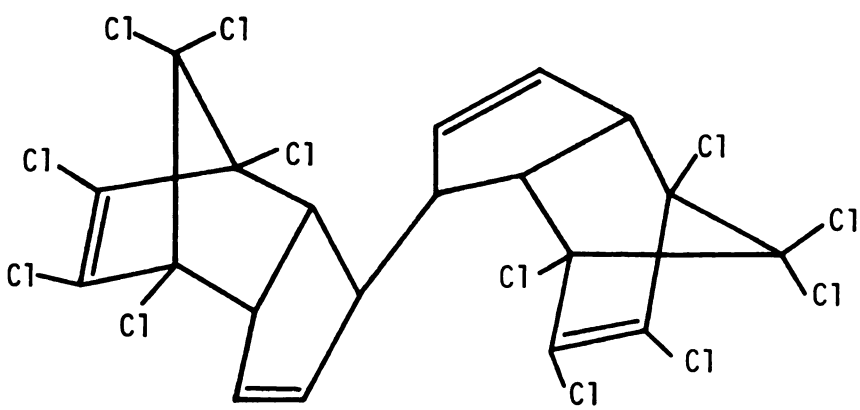

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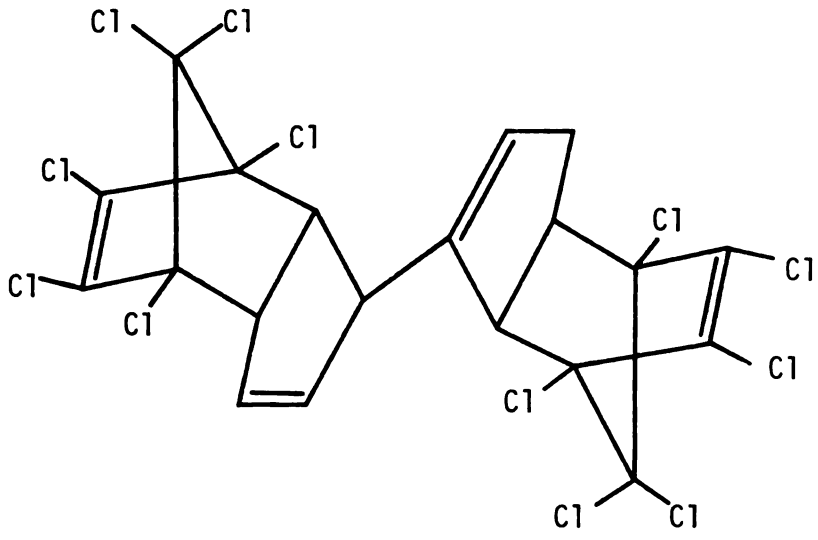

(L)

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By

Janise Louise Ehmann

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To AE and our ISA

ACKNOWLEDGEMENTS

Reflecting back over the time I have spent at the Pesticide Research Center, I can never remember a dull moment in which I have not thoroughly enjoyed my work. I realize that this is due to the fine people with whom I have had the opportunity to be associated with throughout my "learning experience", and there is no way to acknowledge everyone individually.

I would like to thank Dean Leroy Dugan for his sincere interest in my education and the encouragement he gave me to pursue it.

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Axel has been the true life-giving force throughout this period of time.

A special thanks must be extended to Dan and John without who's expertise, concern and humanly love, this work would never have been completed - I owe them my life -.

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INTRODUCTION

Prior to the manufacturing of organic pesticides, treatment of plants for pest control was done by the use of inorganic and natural organic compounds. Wickman (1946) pointed out that the effectiveness of organic chemicals is subject to a number of variables "...causing pesticide inactivation, such as a) mechanical removal by wind or rain; b) volatilization; c) effects as penetration into the interior of the fruit, occlusion in the apple waxes or simple attenuation of the deposit as the apple grows and d) decomposition from the action of sunlight or contact with other substances...". Twenty years later Roburn, 1963, was the first investigator to demonstrate that indeed one of Wickman's postulates was correct, when he observed the appearance of an unidentified compound following dieldrin treated herbage that was left in the field during the summer.

Many investigations in the past have been primarily concerned with photolysis of pesticides under laboratory conditions, either as films on a variety of surfaces under artificial light or indirect sunlight, or in solution and artificial light (Tables 1 and 2). The photoproducts formed were then considered photoproducts of the parent compound which might be found under field conditions. Since Roburn's qualitative findings, much of pesticide photochemistry has dealt with products derived under laboratory conditions. Actual environmental studies of pesticide-epicuticular wax interaction is fragmentory and thus largely hypothetical. The presence of pesticides and/or their residues in the environment is a complex and highly unresolved problem.

In this study a model system was used to examine the photochemical interaction of the insecticide, heptachlor, with the waxy surface of the tomato fruit, or in combination with each of several major chemical constituents of the wax. A considerable amount of photochemistry of heptachor has been elucidated (Flotard, 1968; McGuire, 1969). More recently Baker (1974) has studied the chemistry of the epicuticular wax of the tomato fruit. Our aim was to study the interaction between heptachlor and the epicuticular layer. The epicuticular layer is the first barrier the pesticide has to cross, and in the process of penetration may interact with chemical constituents of the layer.

HISTORICAL REVIEW OF PHOTOCHEMISTRY

Photochemical reactions of organic materials have been known since ancient times. The early Greeks and Romans recognized that dye-stuffs faded when left in the sun, and that the sun is essential for the growth of plants.

The quantitative study of photochemical reactions emerged with the formulation of the first law of photochemistry by Grotthus in 1817, that states "only that light absorbed by a molecule can result in a chemical reaction". Approximately a century later Stark (1908-1912) and Einstein (1912-1913) postulated the second law of photochemistry: "one quantum (photon) of light is absorbed for each molecule altered". This applies only to primary photochemical processes, the production of an excited molecular species. Accordingly radiant energy is transmitted as discrete units called quanta (or photons); this energy of excitation is directly related to wavelength of light and the molecular species excited at that wavelength. This law can best be expressed by the following equation: $E=H_v=\frac{hc}{v}$, where E is the energy of one photon (kcal/erg/sec), h= Plank's constant (6.62×10^{-27}), c= the velocity of light (3×10^{8}m/sec), v= the frequency of radiation. From this equation it is then possible to determine the energy imparted to a molecule at a particular wavelength. However, Bodenstein and co-workers (1913) determined that many photochemical reactions failed to follow the Stark-Einstein law. Instead, they found that many times photochemical reactions produce more than one molecule of product per quantum absorbed, or less than one molecule. These

findings resulted in a revision of the second law of photochemistry, which is now expressed as the quantum yield

$$\Phi = \frac{\text{number of molecules of reactant consumed}}{\text{number of photon absorbed}} .$$

This equation now accounts for photochemical reactions such as those which do not photochemically decompose because they fail to absorb light at a particular wavelength, or molecules that fail to undergo rapid dissociation because their excited states are quite stable and long-lived. This also takes into account those photochemical processes which may require only one photon of absorbed radiation per molecule; however the product yield depends on secondary reactions. A value of zero indicates that no photochemical reaction took place, while a value of one means that all molecules formed photoproducts. However, chain reactions can lead to a value higher than one.

Following the development of quantum theory and understanding of the energy transfer and the electronic transitions which occur following the absorption of light, it is necessary for the molecule to absorb at its wavelength of excitation, and this absorption generally follows Beer's law ($I-I_0 10^{-Ebc}$). This states that the amount of light absorbed at a particular wavelength is directly proportional to the absolute concentration of the absorbing material.

PHOTOCHEMICAL FUNDAMENTALS

The overall photochemical reaction consists of both primary and secondary reactions. The primary process involves the absorption of a quantum of energy by a molecule resulting in an excited state. This absorbed energy can lead to intramolecular rotation, vibration or an altered electronic configuration. This transition from the ground state (E_0) to the excited state results in the disappearance of this molecule via chemical formation of a free radical, carbonium ion, carbanion, intramolecular rearrangement, and or interaction of the excited molecule with a reactant molecule. The excited molecule can also convert back to its initial ground state; that is to say that all reactions are dependent upon the molecular environment. The process involves the excitation of an electron to a bonding or an anti-bonding orbital and the production of an excited state. Two spin configurations are possible: if there is complete spin retention of the paired electrons, this excited state is referred to as the excited singlet (S_1). If the electrons spin are unpaired the resulting configuration is referred to as the excited triplet state (T_1) which is of a lower energy level than the (S_1) state. The excitation to S_1 can also give rise to non-radiative transitions between states of different multiplicity; ($S_1 \rightarrow T_1$). This transition is referred to as intersystem crossing and the chemical products arising from T_1 may or may not be the same as those arising from S_1. Chemical products can be produced from S_1 and/or T_1 . When no reaction occurs during this highly reactive time, these excited molecules tend to rapidly return to their ground

state. The singlet state loses its excited energy as fluoresence. If no reaction occurs during the lifetime of the triplet state its energy will be lost as phosphorescence to its ground state.

Secondary photochemical reactions are non-photochemical reactions driven by energy absorbed by a "sensitized molecule" [A] and transferred to a receptor molecule [B], which can then undergo a number of reactions, depending upon the environment, such as elimination, decomposition (alteration), addition, abstraction, substitution, induced chain reactions, isomerization and dimerization.

PHOTOCHEMISTRY OF CHLORO-CARBON AND CYCLODIENE INSECTICIDES

Investigation of the solid state photolysis of both the chlorocarbon and the cyclodiene insecticides is well documented. Beginning with Gunther's (1945) suggestion that the ultra-violet radiation from sunlight could serve as a catalyst in DDT "degradation" under field conditions there have been many investigations. The work of Wickman (1946), Linquist (1946) and Fleck (1948) established the basis for future photochemical works.

Several photochemically induced reactions are common to both classes of insecticides, when irradiated as films (Tables 1 and 2). Dechlorination occurs with DDT, (Table 1; XVI Methoxychlor, Table 2; XX) and a variety of polychlorinated biphenyls (PCB's), (Table 1; XXIII, XXVI, XIX, XXXI, XXXV), in the class of chlorocarbon pesticides. Mirex, (Table 2; LXIII) is the only cyclodiene pesticide reported to dechlorinate as a film. Dehydrohalogenation of DDT (Table 1; XVI) to DDE, (Table 1; XVII) and Methoxychlor (Table 1; XX) to its olefin analogue (Table 1; XXII) have also been reported to occur in the solid state. Oxidations also commonly occur with DDE, in which the di-chloromethyl group of the DDT molecule is lost and oxygen is replaced to form DD=O(p,p' di-chloro biphenyl benzophenone) (Table 1; XVIII). Oxidation has also been reported for a number of cyclodiene compounds, namely Aldrin (Table 2; XLVI) and Heptachlor (Table 2; VI) which are oxidized to their epoxide forms. Alley (1974) reported that with Mirex dechlorination occurred first, followed by oxidation to its ketone analogue (Table 2 ; LXXVI); then tautomerization

Table 1. Solution and film photolysis of chloro-carbon pesticides.

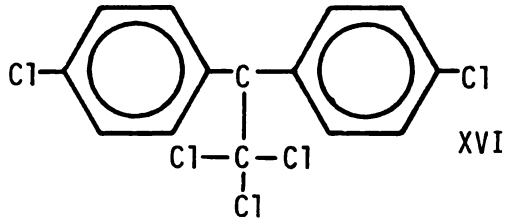
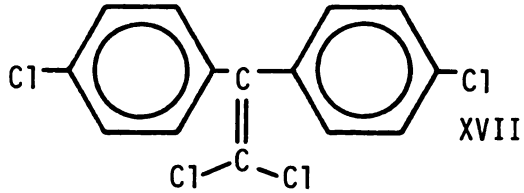
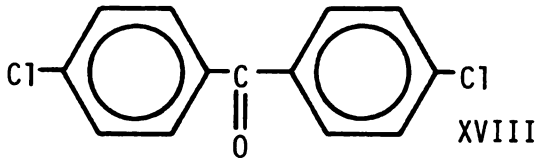
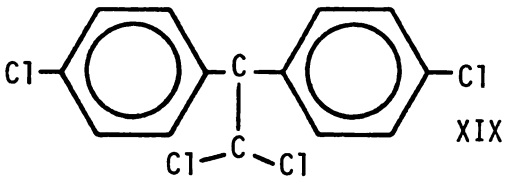
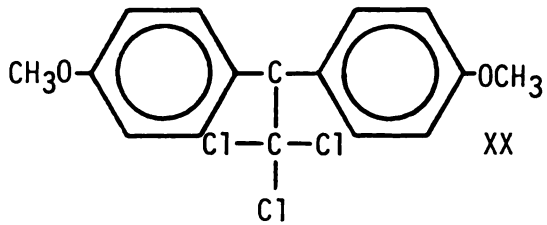
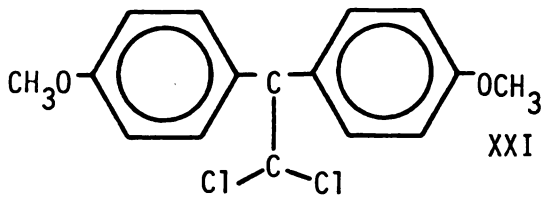
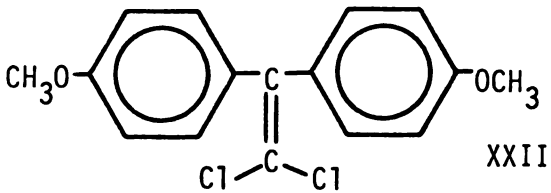
Compound	Conditions	Photoproduct(s)	Reference
 XVI	310 nm, 1.5 hrs, cyclohexane + amine inducer	 XVII	Miller (1969)
	254 nm, ethanol + oxygen	 XVIII	Fleck (1948)
	254 nm, 1 hr, hexane 310 nm, 1.5 hrs, cyclohexane + amine inducer	 XIX	Miller (1969)
 XX	310 nm, 12 hrs, n-heptane	 XXI	Mac Niel et al. (1972)
		 XXII	Mac Niel et al. (1972)

Table 1. Continued.

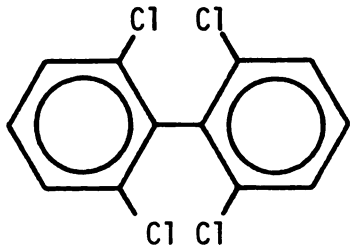
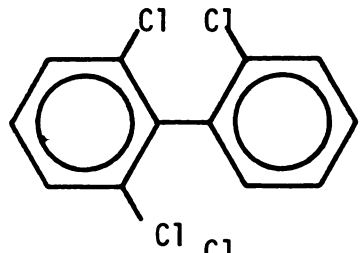
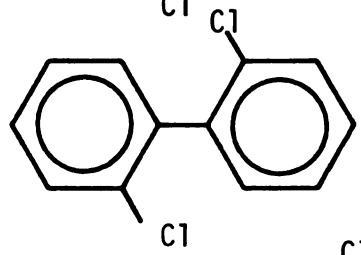
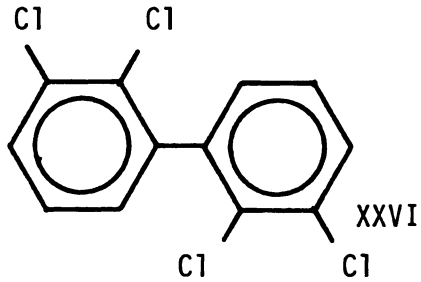
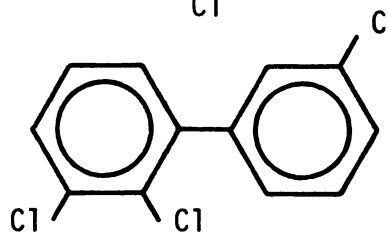
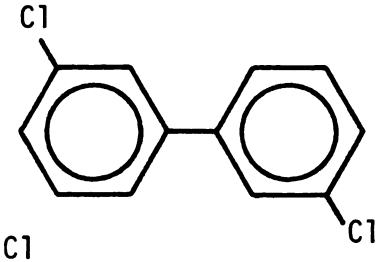
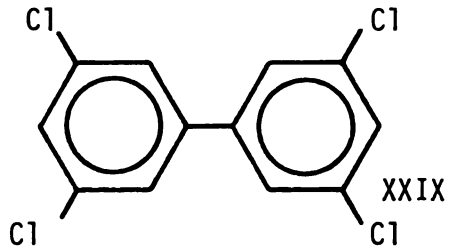
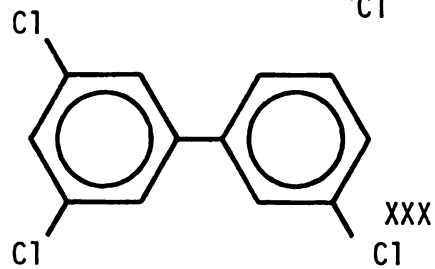
Compound	Conditions	Photoproduct(s)	Reference
 XXIII	310 nm, 10-15 hrs, hexane	 XXIV	Ruzo et al. (1974)
		 XXV	Ruzo et al. (1974)
 XXVI	310 nm, 10-15 hrs, hexane	 XXVII	Ruzo et al. (1974)
		 XXVIII	Ruzo et al. (1974)
 XXIX	310 nm, 10-15 hrs, hexane	 XXX	Ruzo et al. (1974)

Table 1. Continued.

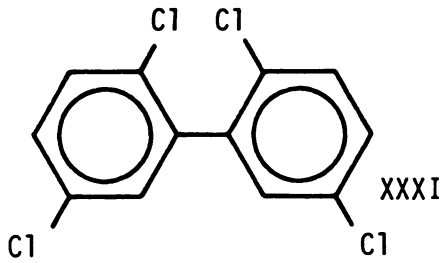
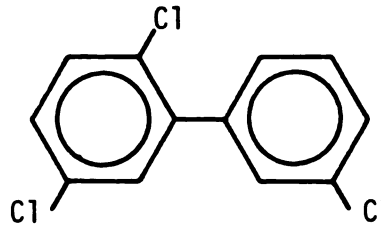
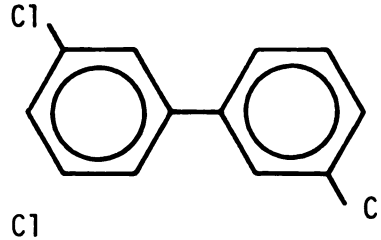
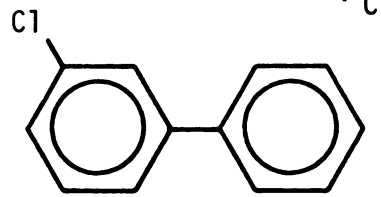
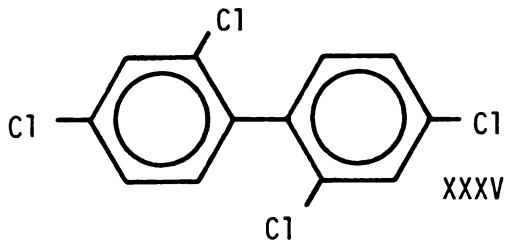
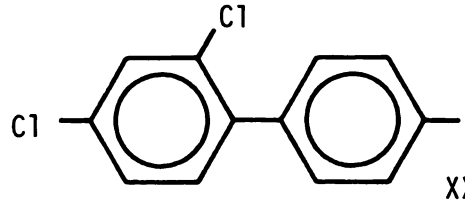
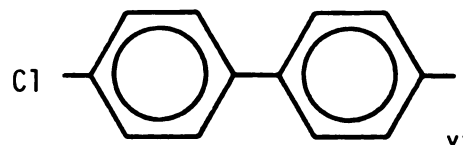
Compound	Conditions	Photoproduct(s)	Reference
 XXXI	310 nm, 10-15 hrs, hexane	 XXXII	Ruzo et al. (1974)
		 XXXIII	Ruzo et al. (1974)
		 XXXIV	Ruzo et al. (1974)
 XXXV	310 nm, 10-15 hrs, hexane	 XXXVI	Ruzo et al. (1974)
		 XXXVII	Ruzo et al. (1974)

Table 1. Continued.

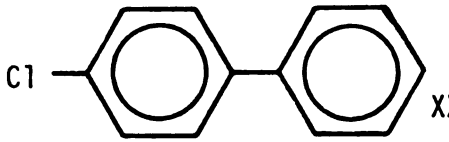
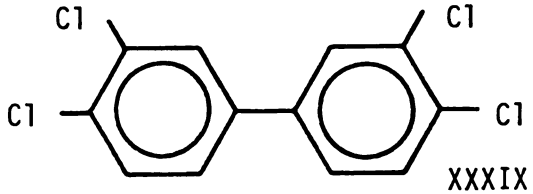
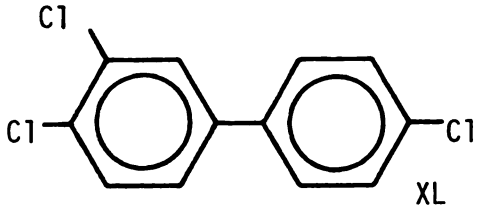
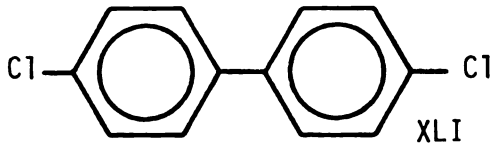
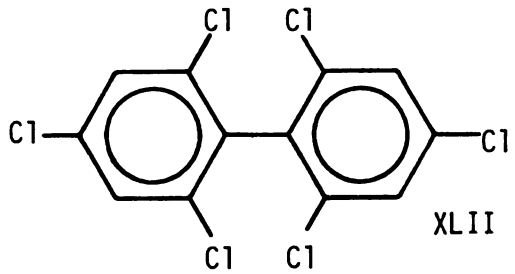
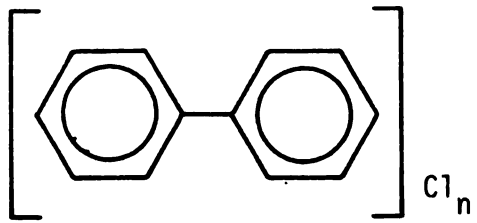
Compound	Conditions	Photoproduct(s)	Reference
		 XXXVIII	Ruzo et al. (1974)
 XXXIX	310 nm, 36 hrs, hexane	 XL	Ruzo et al. (1972)
		 XLI	Ruzo et al. (1972)
 XLII	310 nm, 4 days, hexane or methanol	 (and oxygenated chlorobiphenyls) XLIII	Safe and Hutzinger (1970) n = 1,2,3,4,5

Table 2. Solution and film photolysis of cyclodiene pesticides.

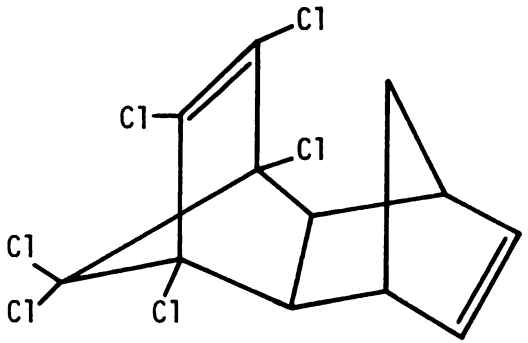
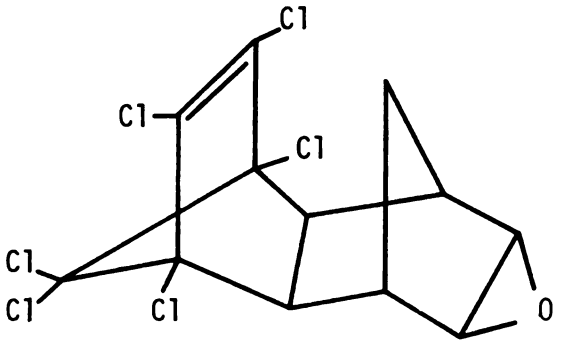
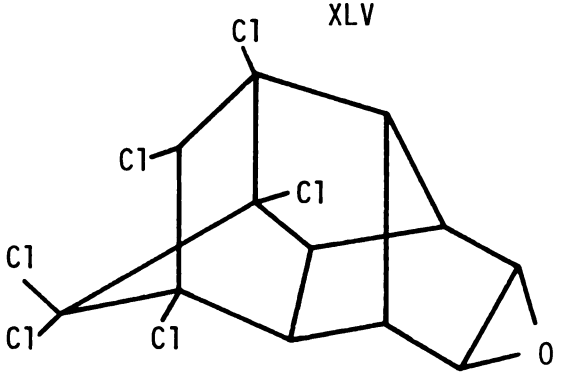
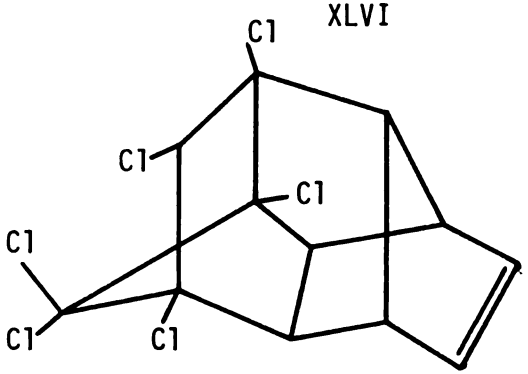
Compound	Conditions	Photoproduct(s)	Reference
 XLIV	sunlight (290-310 nm) 1 month, film	 XLV	Rosen and Sutherland (1969)
	sunlight (290-310 nm) 1 month, film	 XLVI	Rosen (1967)
	254 nm, 7 days, ethyl acetate		Rosen and Carey (1968)
	254 nm or 310 nm, 21 hrs, benzene + benzophenone		Fisher and Korte (1969)
	sunlight (290-310 nm) 7 days, film	 XLVII	Rosen and Sutherland (1969)

Table 2. Continued.

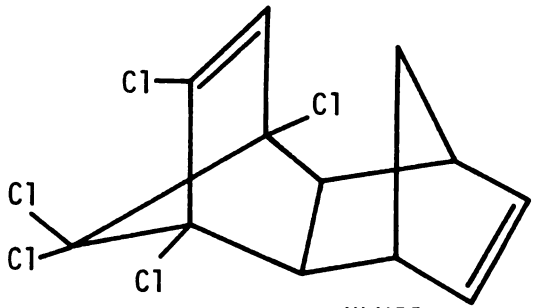
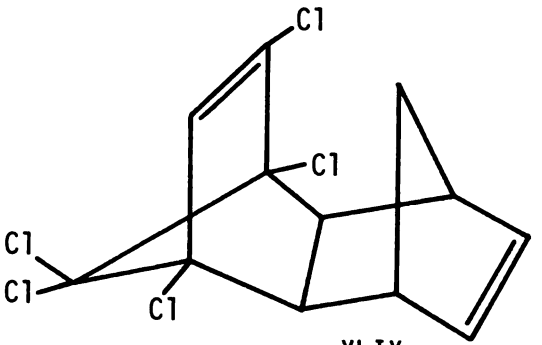
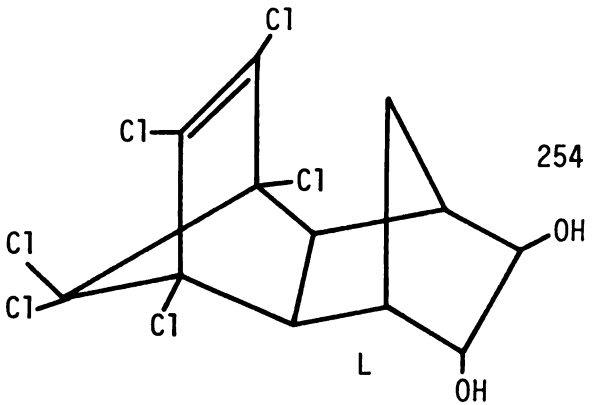
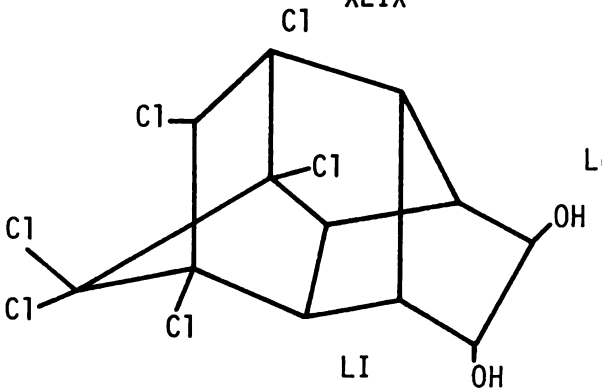
Compound	Conditions	Photoproduct(s)	Reference
	254 nm, 7 days, ethyl acetate 280 nm, 8 hrs, hexane or cyclohexane or methanol	 XLVII	Rosen (1967) Henderson and Crosby (1967)
	254 nm, 24 hrs, ethyl acetate	 XLIX	Rosen (1967) Henderson and Crosby (1967) Henderson and Crosby (1967)
 L	254 nm, 24 hrs, film	 LI	Lombardo et al. (1972)

Table 2. Continued.

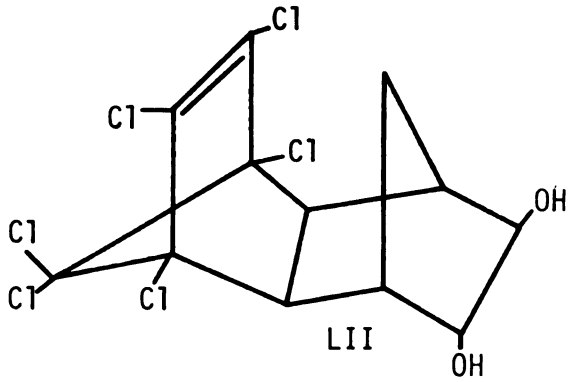
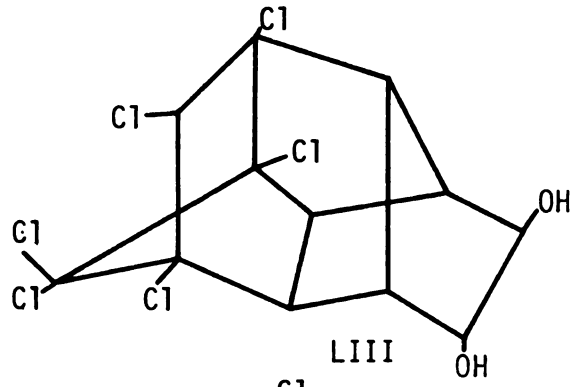
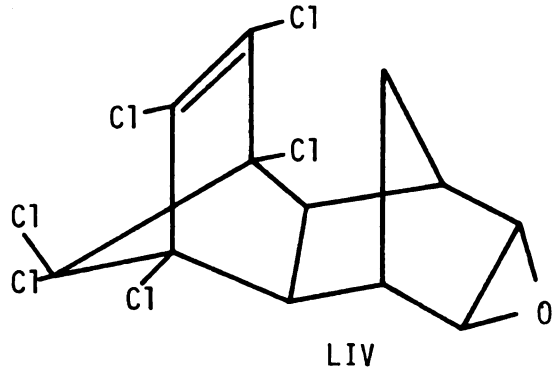
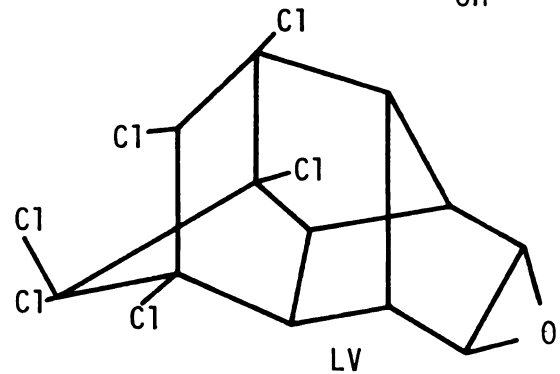
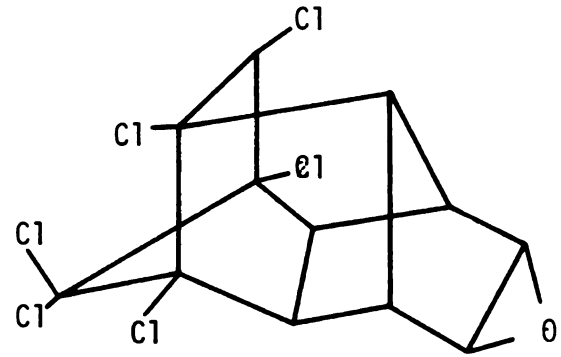
Compound	Conditions	Photoproduct(s)	Reference
 LII	254 nm, 24 hrs, film	 LIII	Lombardo et al. (1972)
 LIV	254 nm, film on paper, 30 min. 254 nm, 48 hrs, ethyl acetate 254 nm, 48 hrs, hexane	 LV	Robinson et al. (1966) Rosen et al. (1966) Henderson and Crosby (1967a)
		 LVI	Robinson et al. (1966) Rosen et al. (1966) Henderson and Crosby (1967a)

Table 2. Continued.

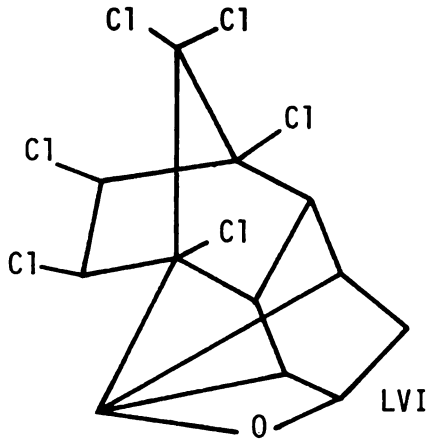
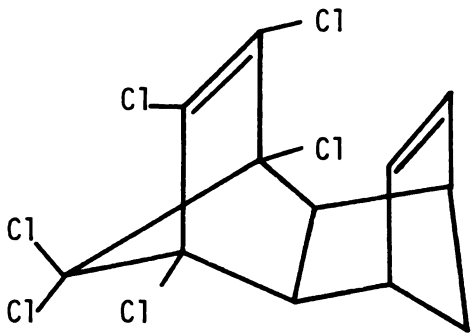
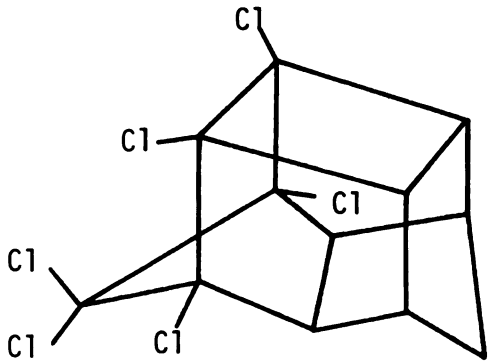
Compound	Conditions	Photoproduct(s)	Reference
	254 nm, 1-24 hrs, ethyl acetate	 LVII	Benson (1971)
	254 nm, acetone		Fisher and Korte (1969)
 LVIII	(no conditions given)	 LIX	Cookson and Grundwell (1958)
	254 and 310 nm, 1-2 hrs, hexane		Zabik et al. (1971)

Table 2. Continued.

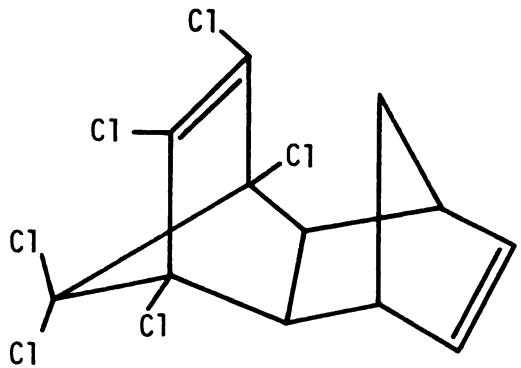
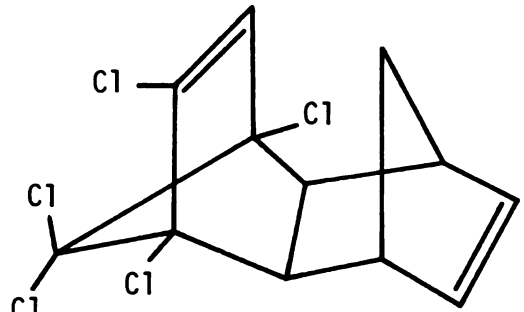
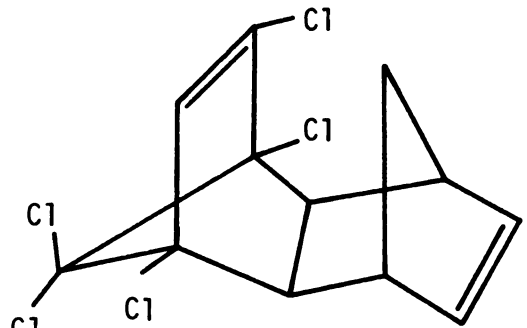
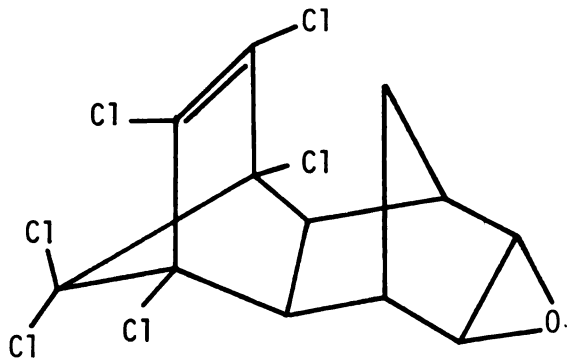
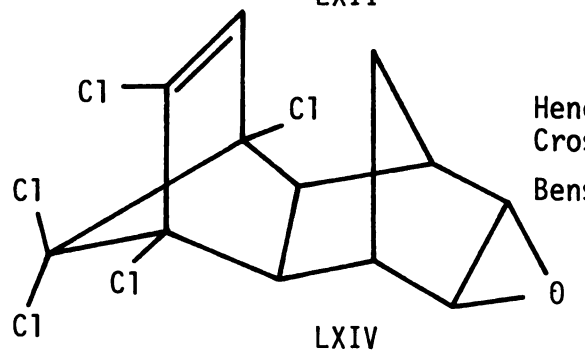
Compound	Conditions	Photoproduct(s)	Reference
 LX	254 nm, 7 days, ethyl acetate 280 nm, 8 hrs, cyclohexane 254 nm, 24 hrs, ethyl acetate	 LXI	Rosen (1967) Henderson and Crosby (1967) Benson (1971)
		 LXII	Rosen (1967) Henderson and Crosby (1967) Benson (1971)
 LXIII	254 nm, hexane 254 nm, 1-24 hrs, ethyl acetate	 LXIV	Henderson and Crosby (1969) Benson (1971)

Table 2. Continued.

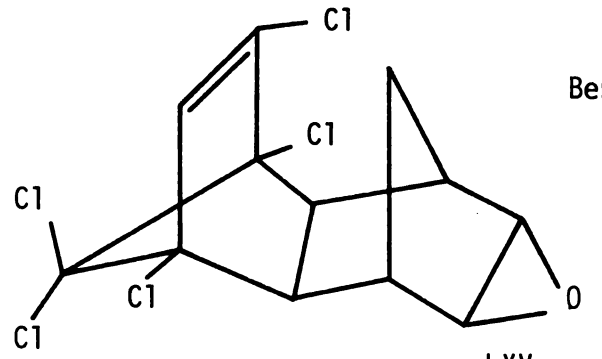
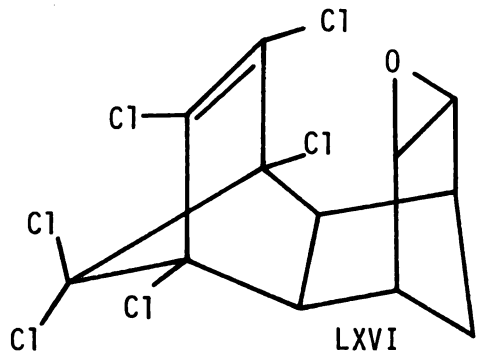
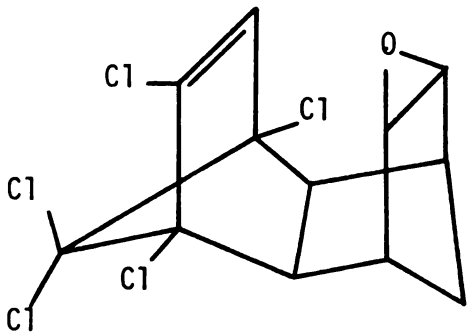
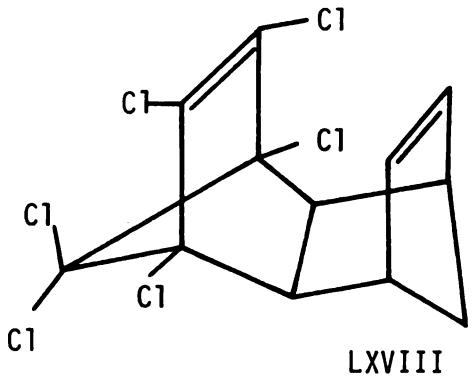
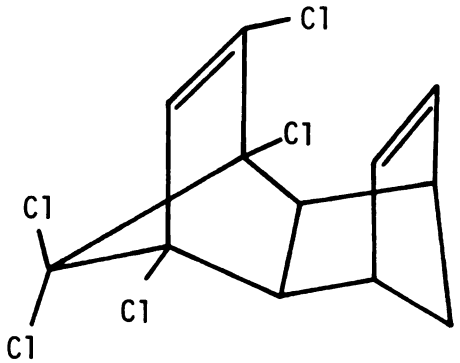
Compound	Conditions	Photoproduct(s)	Reference
 LXV			Benson (1971)
 LXVI	310 nm, 1-2 hrs hexane	 LXVII	Zabik et al. (1971)
 LXVIII	254 nm, 12 hrs, hexane	 LXIX	Zabik et al. (1971)

Table 2. Continued.

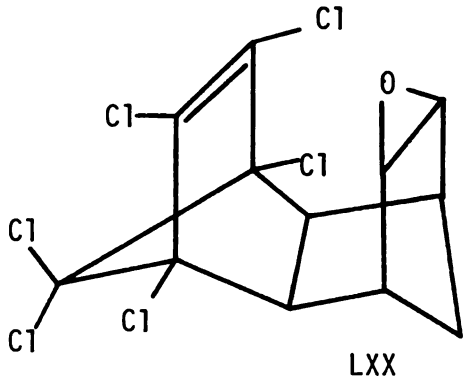
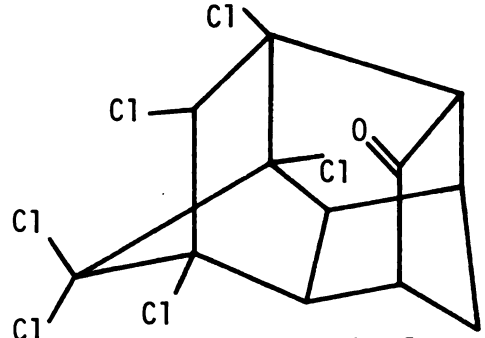
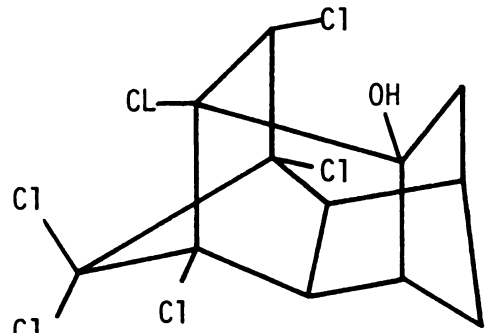
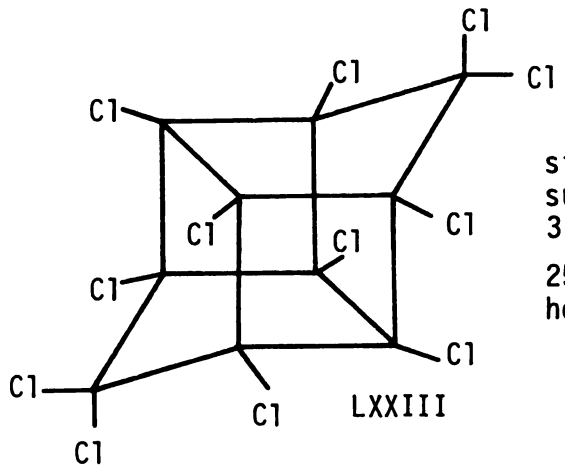
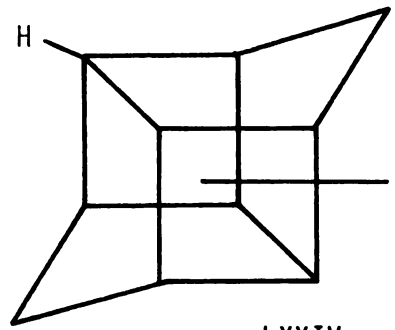
Compound	Conditions	Photoproduct(s)	Reference
 LXX	254 nm, 48 hrs, film 254 or310 nm, 1-2 hrs, hexane	 LXXI	Rosen, Sutherland and Lepton (1966) Zabik et al. (1971)
		 LXXII	Rosen, Sutherland and Lepton (1966)
 LXXIII	silica gel deposits, sunlight (290-310 nm) 3 months 254 nm, 48 hrs, cyclo-hexane	 LXXIV	Gibson (1972) Alley et al. (1973)

Table 2. Continued.

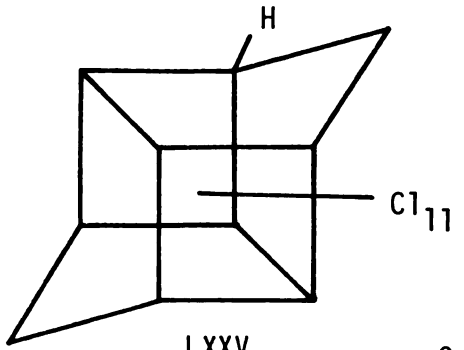
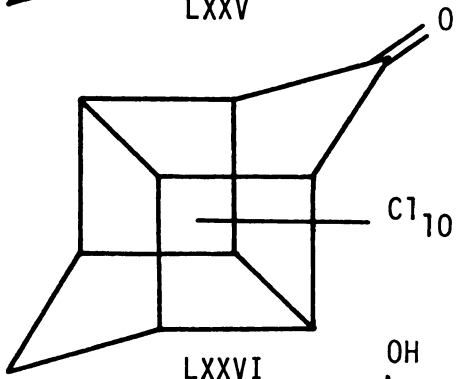
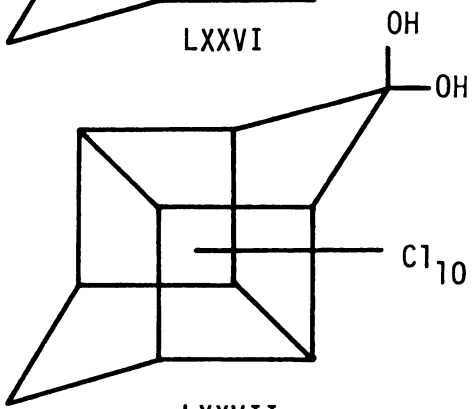
Compound	Conditions	Photoproduct(s)	Reference
		 LXXV	Gibson (1972) Alley (1973)
	silica gel deposits, sunlight (290-310 nm, 3 months	 LXXVI	Alley et al. (1973) Ivie et al. (1974)
		 LXXVII	Ivie et al. (1974)

Table 2. Continued.

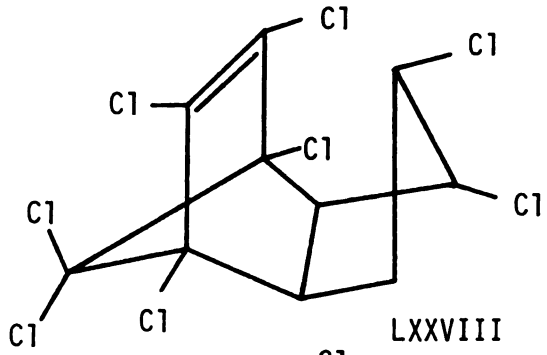
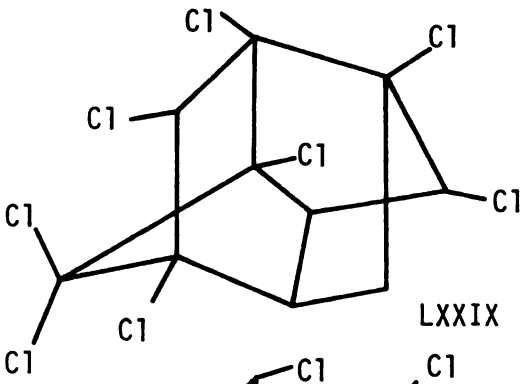
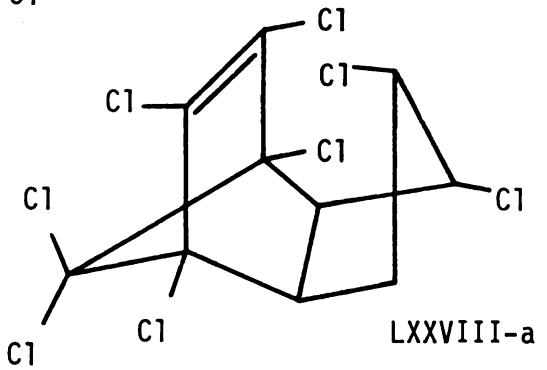
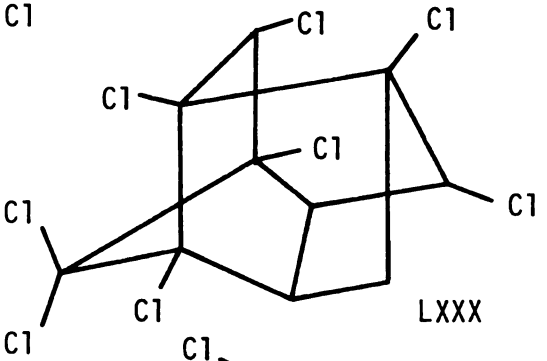
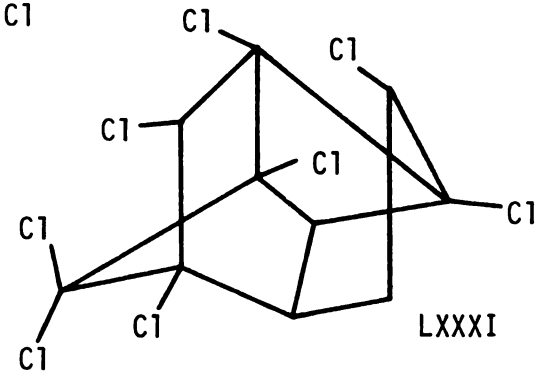
Compound	Conditions	Photoproduct(s)	Reference
 LXXVIII	254 nm, film, 16 hrs, sunlight (290-310 nm), 46 hrs, film	 LXXIX	Vollner and Korte (1969)
	254 nm, 36 hrs, water, acetone		Ivie et al. (1974)
	254 nm, 16-20 hrs, water, dioxane or methanol		Fisher and Korte (1969)
 LXXVIII-a		 LXXX	Vollner and Korte (1969)
			Ivie et al. (1974)
			Fisher and Korte (1969)
	sunlamp (310 nm), 24 hrs	 LXXXI	Ivie et al. (1974)

Table 2. Continued.

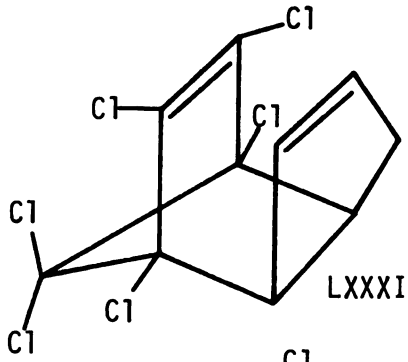
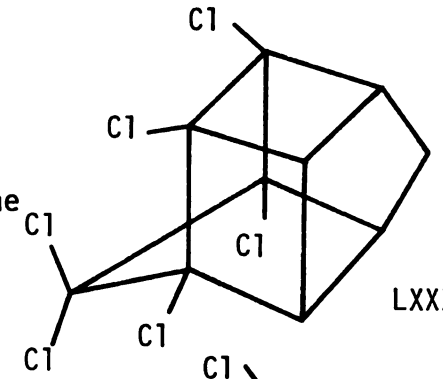
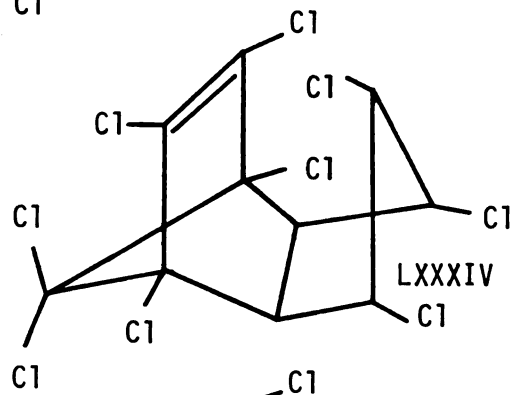
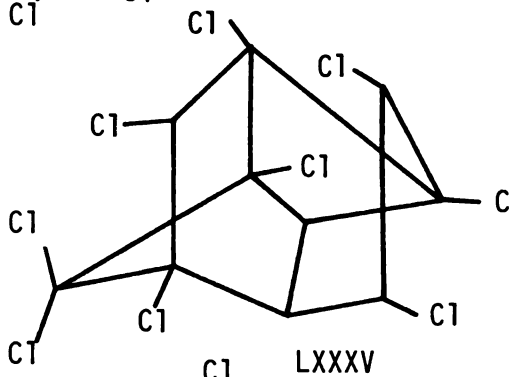
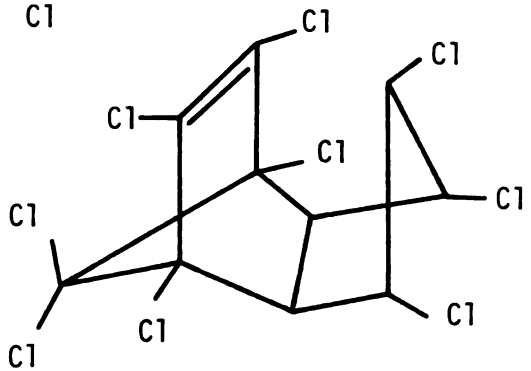
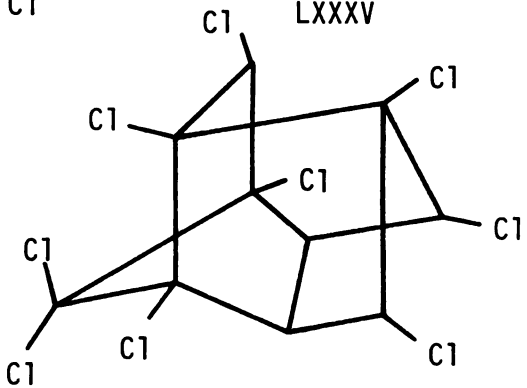
Compound	Conditions	Photoproduct(s)	Reference
 LXXXII	film (no conditions given) sunlamp (310 nm), 24 hrs, 210 nm, 60 hrs, acetone	 LXXXIII	Vollner and Korte (1969) Benson et al. (1971)
 LXXXIV	sunlight, film, (290-310 nm) 4 hrs 310 nm, 64 hrs, acetone	 LXXXV	Ivie et al. (1972) Vollner and Korte (1969)
 LXXXIV-a	300 nm, acetone	 LXXXVI	Ivie et al. (1972)

Table 2. Continued.

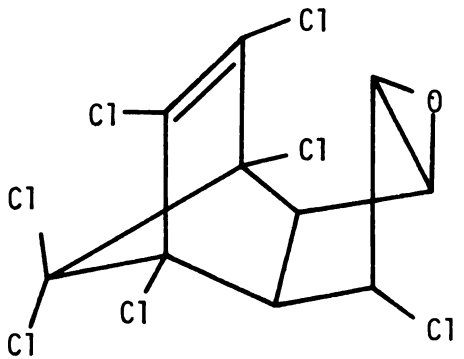
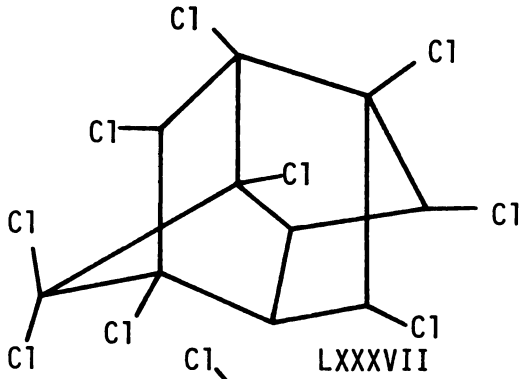
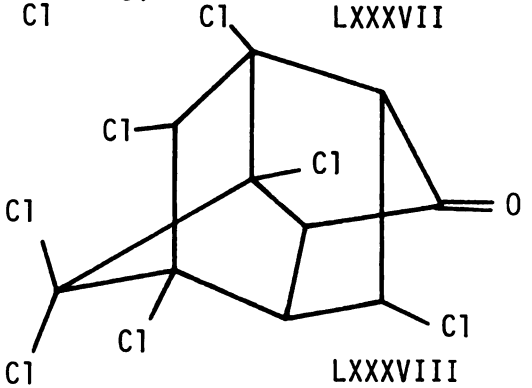
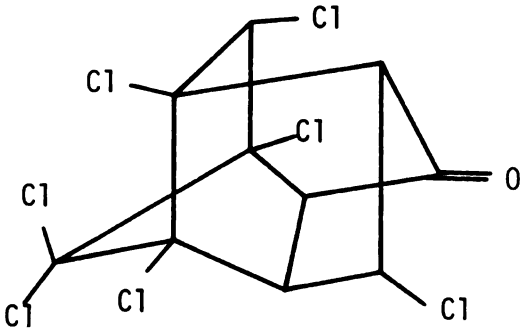
Compound	Conditions	Photoproduct(s)	Reference
 VI	254 nm or sunlight (290-310 nm), film, 1-24 hrs Corex or Kimax, 1 or 11 hrs, acetone	 LXXXVII	Ivie et al. (1972)
		 LXXXVIII	Fisher and Korte (1969) Benson (1971) Graham (1973) Ivie et al. (1972)
		 LXXXIX	Fisher and Korte (1969) Benson (1971) Graham (1973) Ivie et al. (1972)

Table 2. Continued.

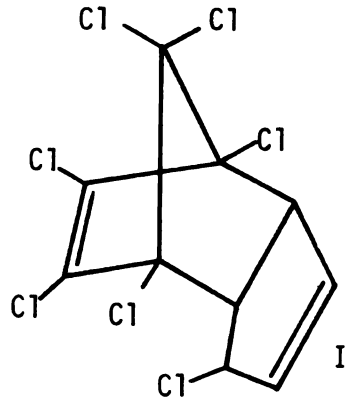
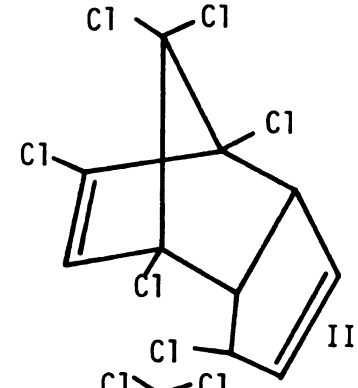
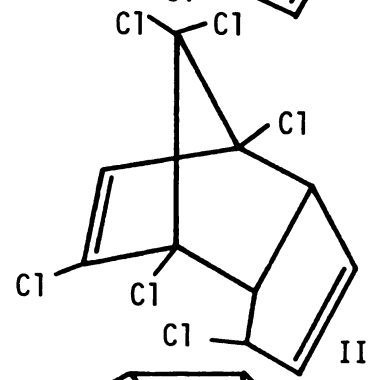
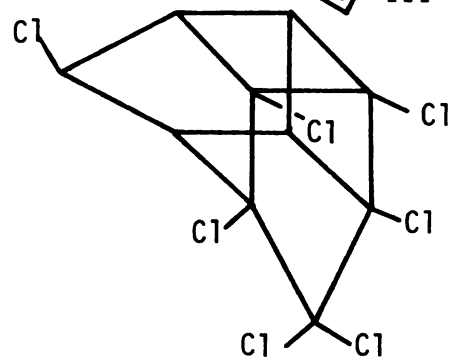
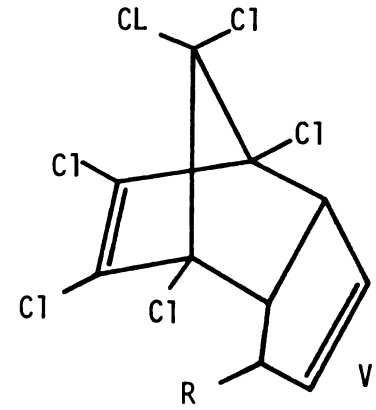
Compound	Conditions	Photoproduct(s)	Reference
 I	254 nm, 3 hrs, hexane or cyclohexane	 II	McGuire (1969) Flotard (1968)
		 III	McGuire (1969) Flotard (1968)
	solid film or in acetone	 IV	Fisher and Korte (1968)
	solid film, 254 nm, 16-20 hrs		Vollner and Korte (1969)
	254 nm, 36 hrs, water, methanol		Benson (1971)
	280 nm, 2 hrs, acetone		Rosen et al. (1969)
	310 nm, 21 hrs, benzene + benzophenone		McGuire (1969)
	310 nm, 3 hrs, acetone		Flotard (1968)

Table 2. Continued.

Compound	Conditions	Photoproduct(s)	Reference
	310 nm, hexane or cyclopentane or ethyl acetate	 R=hexyl cyclopentyl ethylacetyl	Mc Guire (1969)

to its diol form (Table 2; LXXVII). Complete photochemical reduction/ oxidation of Dieldrin and photo-Dieldrin to CO_2 and HCl has also been reported (Gäb et al., 1974). Isomerization, however, is the most prominent photochemical reaction common to the cyclodiene class of insecticides. Depending upon the parent compound, the photoisomer will either be a half or the Weinstein full cage form (Table 2; XLVI; XLVII; LI; LIII, LV, LVI, LVII, LIX, LXXI, LXII, LXXIX, LXXX, LXXXI, LXXXIII, LXXXV, LXXXVI, LXXXVII, LXXXVIII, LXXXIX, IV).

The photochemical reaction and product formation common to both classes of insecticides is similar and/or the same when photolyzed in solution or as films. Dechlorination occurs more frequently in solution for both classes of compounds. Photodechlorination of tetrachlorobiphenyl compounds occurs step-wise with the successive loss of chlorine atoms (Ruzo, 1974). On photolysis in a polar solvent the substitution of individual chlorine atoms by the anionic portion of the solvent occurs. The photodechlorination of the cyclodienes to their hexa-and penta-chloro derivatives is a common reaction of this class of pesticides (Table 2; XLIX, LXI, LXII, LXIV, LXV, LXIX, II, III) with the exception of cis and trans Chlordane, Nonachlor, and Heptachlor epoxide.

Oxidation has been reported for a number of chloro-carbon pesticides in solution. Miller (1969) reported 16% conversion of DDT to DD=O (Table 1; XVIII) Plimmer (1969) has postulated the conversion of DD=O (Table 1; XVIII) to 2,2 bis (p-chlorophenyl)acetate. Substitution has also been reported to occur in hydrocarbon solvents in which the chlorine atom is replaced by a hydrogen atom. Such is the case for Mirex (Table 2; LXXIV, LXXV). However, the most common photochemical reaction for the norbonyl compounds in solution is that of photo-isomerization: the photoproducts, in most cases, are the same as those observed in film photolysis. The

only other reaction peculiar to this class of compounds was the solvent addition to the allyl position of Heptachlor (Table 2; V) (McGuire,1969).

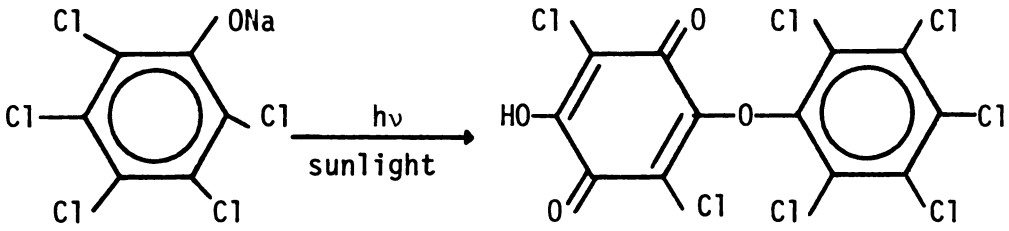
Photo-isomerization of the cyclodiene insecticides is due to intra-molecular bridging, which results either in the more common half cage isomeric form or the closed cage, observed with Isodrin (Table 2; LIX), Chlordene (Table 2; LXXXIII) and Heptachlor (Table 2; IV), in which these compounds possess an endo-endo configuration. In this case the two double bonds open to permit such intra-molecular closure. The half cage isomer occurs with cyclodiene compounds possessing the exo-endo configuration. The isomer will then have two isomeric possibilities of bridging through intra-molecular hydrogen migration and carbon-carbon bond formation. This is common to Aldrin, Dieldrin, Endrin, cis-Chlordane, cis-Nonachlor and Heptachlor epoxide. It was initially reported that this bridging was not possible with trans-Chlordane since the chlorine atom on the center carbon of the cyclopentane ring is directed inward toward the double bond and the two chlorine atoms on the cyclopentene ring. This structure, therefore, interferes with hydrogen migration and ring closure. Trans-Nonachlor possesses a similar configuration, however, it was reported (Ivie et al., 1972) to isomerize not to its half cage isomer but to a methylene bridged analogue (Table 2; LXXXV).

The photochemical rearrangement of Endrin to its photo-ketone (Table 2; LXXI) is a similar reaction reported to occur with heptachlor epoxide (Table 2; LXXXVIII) (Benson, 1971). This too, involves hydrogen atom migration, followed by rearrangement of the epoxy group to a carbonyl and carbon-carbon bond formation through the double bond.

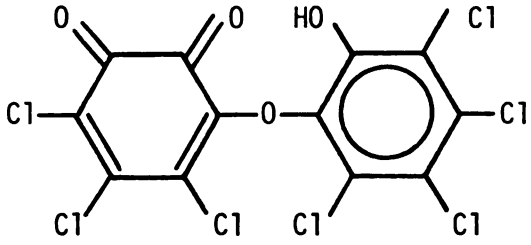
Dimerization is a rarely reported photochemical reaction, but is known to have occurred in certain cases. Wickman (1946) alluded to this

reaction with DDT, "... in which one chlorine atom is removed from the tri-chloromethyl group ($-CCl_3$) and then two residues combine to form the dimer. No data have been collected from irradiation experiments to definitely indicate that such a compound is present in the final product, but it would probably contain a labile chlorine...". Sodium pentachlorophenoxide (Na-PCP), a herbicide used in Japanese rice fields, is highly toxic and easily photo-decomposed within several days following its application (Kuwahara et al., 1965). Its photoproducts have been identified as a series of dimers and trimers (Figure 1). These findings have been verified by chemical, infra-red and mass spectral analysis.

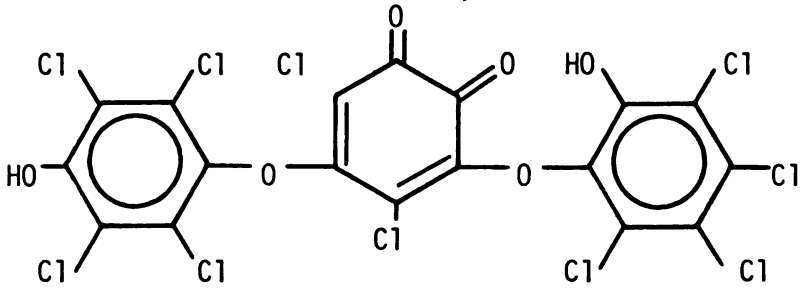
Figure 1. The naturally formed photoproducts following application of sodium pentachlorophenoxide (Na-PCP) to rice fields. (Kuwahara et al., 1965).



2,5-dichloro-3-hydroxy-6-pentachlorophenoxy-p-benzoquinone



3,4,5-trichloro-6-(2',3',4',5'-tetrachloro-6'-hydroxyphenoxy-O-benzoquinone



3,5-dichloro-4-(2,3,5,6-tetrachloro-4-hydroxyphenoxy)-6-(2,3,4,5-tetrachloro-6-hydroxyphenoxy)-O-benzoquinone

NATURE OF THE CUTICULAR MEMBRANE

A. Morphology

Probably the most characteristic feature of the plant cuticle is its extreme variability. Cuticles differ not only chemically, but vary in continuity, degree of perforation and thickness and in the chemical properties between different plants and different environments.

The existence of this outer-most layer of aerial plants first drew the attention of biologists as early as the 17th century. Brongniart (1830) later verified this by means of a simple experiment. He left cabbage leaves in water for a prolonged period of time allowing the cellulose components to disintegrate. He then was able to isolate a continuous, transparent film without appreciable organization. Due to its positive reaction with Sudan stains, which react with materials of a fatty nature, he suggested that this material was composed of cutine", which he later named the cuticle. Since that time more refined and varied chemical methodology has evolved to isolate the cuticle, allowing better study of its morphology, chemistry and allied areas of importance. Due to these early studies the cuticular membrane has been the topic of numerous investigations and the findings the subject of several reviews.

Figure 2 represents a schematic of a typical cuticle with its morphology and chemistry discussed below. Presently, the conventionally accepted concept of the morphology of a typical cuticle is explained by Norris & Bukovac, 1968. On the epidermal cell wall side, the cuticular

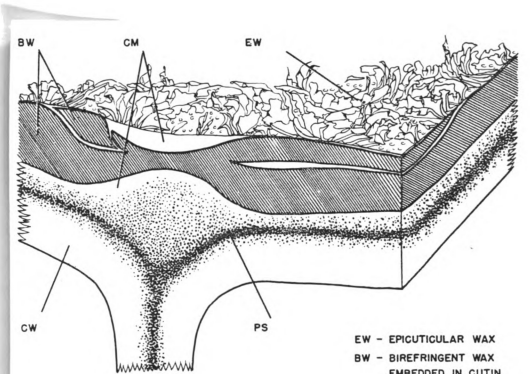


Figure 2. A schematic of a typical cuticle.

membrane may project downward between the anticlinal walls of the epidermal cells. In mature leaves and fruits, oftentimes, the entire epidermal cell may be encapsulated by the cutinization of the cell wall (Baker, 1970). However, in most plants there is not a distinct anatomical or chemical boundry between the various components. Rather, they merge imperceptively into one another and are difficult to distinguish by light or electron microscopy.

The outermost epicuticular wax deposit on the plant surface exists in a specific pattern, which in turn follows the outline of the underlying epidermal cells. The quantity and structural characteristics of wax vary with each plant (Martin and Juniper, 1970) Ameluxen et al., (1967) have recently classified the surfaces waxes into five classes according to their morphological appearance: 1) rodlet form, 2) granular forms, 3) platelet form, 4) layered or encrusted form and 5) the aggregated or semi-liquid form. All these classifications are based upon evidence from fine structure studies.

Cutin, which constitutes the major structural portion of the cuticle, is a highly oriented and complex polymer directly underlying the epicuticular wax. According to Kolattakuty (1973), cutin can constitute between 50 and 90% of the cuticle, depending upon the plant species. The pectin region is considered primarily as cementing the cuticular membrane (composed of cutin, cuticular and epicuticular waxes) to the underlying cell wall. The pectin layer is intercalated to varying degrees with cutinized wax in its uppermost regions and then gradually becomes a distinct region adjacent to the epidermal cells and projecting into the anticlinal walls of these cells. The walls of the epidermal cells consist of cellulose embedded in a matrix of hemicellulose and pectin. The basic structural unit of cellulose is a series of microfibrils each consisting

of 300 to 500 individual cellulose molecules, arranged parallel to each other. The micro-fibril is rectangular, and approximately 8 x 25 nm in size. Between each of the cellulose microfibrils are noncrystalline polysaccharides described as propectin and hemicellulose A and B. Sitte and Rennier (1963) examined the cuticles of a number of species by use of light and electron microscopy. They were able to demonstrate the presence of four layers with changes in densities from the surface wax, through the cutin and pectin regions, to the cellulose of the periclinal walls of the epidermal cells.

B. Chemistry

In recent years the chemical nature of the plant cuticle has received considerable attention. Much of the chemistry of the cuticular membrane and underlying regions has been elucidated by means of a wide variety of modern analytical techniques, in particular, gas chromatography or combined gas chromatography - mass spectroscopy, many times with computer assistance.

Epicuticular Waxes

The epicuticular waxes are a complex mixture of long chain alkanes, primary and secondary alcohols, ketones, aldehydes, fatty acids, esters and a variety of triterpenoid compounds (Kolattakuty & Walton, 1973). For the most part, all classes of surface waxes consist of a homologous series of compounds with predominant chain lengths from 21-37 carbons. The most common parafins are n-alkanes with an average chain length from 25-33 carbons. These compounds, along with ketones, and secondary alcohols all consist of odd numbers of carbon atoms. The fatty acids, primary alcohols and aldehydes all generally posses even numbered carbon

chains. The acids may exist free or as esters, with varying chain lengths between 10-30 carbons. Small quantities of olefins have been found, the chain lengths are the same as for the alkane fraction. The position of the double bond may vary, occurring between carbons, 1,2,3,5, 7,9, or 10. Cyclic components, in particular pentacyclic tri-terpenoids are the most common, however some aromatic hydrocarbons have been isolated. There is little information about the distribution and orientation of these chemical constituents within the wax layer.

Cutin Chemistry

Attempts to unravel the chemistry of cutin began early in the 19th century with Brongniart (1830) and Fremyand Urbain (1882). These early investigators employed classical chemical techniques and successively isolated "cutose" from Agrave, a moncot. It consisted predominately of stearocutic and oleacutic acids. These compounds were thought to be the two predominent components of cutin. Several years later, cutose was renamed cutin and was shown to contain approximately 77% ester type bonds, 22% peroxide bridges and 1% ether bonds.

In a review by Kolattakuty and Walton (1973) the major components of cutin were classfied into three chemical groupings: a) non-hydroxylated fatty acids; cutin with this basic chemical composition is poorly developed and quite fragile, b) di- and tri-hydroxylated fatty acids with chain lengths of 15,16 and 18 carbons; such hydroxylated fatty acids containing two or three hydroxyl groups on carbons 9,10 and 18 constituents of a thicker cross-linked cutin. It is quite apparent that the greater the number of hydroxyl groups at the proper position on the molecule, the greater the degree of polymerization in cutin and consequently the greater its strength. The chemistry of cutin is now known and is

constant throughout the plant kingdom.

Cutin is a polymol-cular network of cross-esterified carboxylic and hydroxy-carboxylic acids; some peroxide and ether bonds also interconnect the fatty acid backbone. However, the primary components are 9,10,18 trihydroxyoctacecanoic acid and 10,16 dihydroxyhexadecanoic acid. Infra-red spectroscopy shows the presence of some free hydroxyl groups since there is a preponderance of hydroxyl groups in comparison to carboxyl groups.

Since a portion of the polar groups remain free during the polymerization of cutin, it is a semi-lipophilic molecular network and therefore has the capacity of swelling in the presence of moisture, permitting transpiration and absorption of water soluble substances. Cutin, therefore is both hydrophobic and hydrophilic due to its unique chemical properties.

Pectin and Cellulose Chemistry

The chemical composition of pectin is that of long chain polygalacturonic acids(poly-uronides), having some side carboxyl groups. Some of the carboxyl groups are methylated. These substances exist in an amorphorous state and are responsible for the properties of strong water retention.

Cellulose is a β 1→4 glucan in which each glucose molecule is rotated 180 degrees to its neighbor chain. The hydroxyl groups of a cellulose chain are oriented outward, rendering the linkage to other adjacent molecules. Linkage with proteins may also occur within this matrix and are chemically defined as carbohydrates that unlike cellulose contain uronic acid residues. Hemicellulose molecules are also present.

FACTORS INFLUENCING THE FOLIAR SORPTION AND RETENTION OF CHEMICALS

The physical and chemical properties of the cuticle and the penetrating chemical determine the extent to which the chemical will penetrate the cuticle. The stereochemistry, polarity, net charge of the applied molecule are some of the more important parameters influencing the compound behavior. There exists, therefore, a complex series of events which can singly or in combination influence any interaction between the chemical and the cuticular barrier.

Agricultural chemicals can be applied to plants for the control of pests, to regulate growth, to supply nutrients, etc. Variables within a plant species may directly affect the retention and transport within the plant.

The epicuticular wax layer, from its development to its mature form constitutes one important factor in the phenomenon of cuticular-chemical interaction. Ebeling (1964) pointed out that the plant surface is directly influenced by 1) plant form (erect or spreading), 2) leaf shape (broad or narrow), 3) leaf position and density (horizontal or upright) and, 4) leaf surface margins (hairy, waxy, sculptured). Ebeling noted that only very minute amounts of sprayed chemicals adhere to narrow, upright leaves or to highly waxy surfaces.

Although plant surfaces vary in chemical composition, all foliage is covered by a waxy material; and like all plant structures, the cuticle undergoes ontogenetic changes. During its development it is quite fluid

and theoretically more reactive. As it matures, it gains in thickness and the degree of surface oxidation and becomes more highly polymerized.

The cuticular surfaces of a large number of plant species have been shown to posses fine structure (in many cases referred to as "bloom") which may be characteristic for a given plant. Trichomes may also be present. Such features may play a role in pesticide-dose interaction with the plant surface.

The variations in the chemistry and morphology of the plant surface then may directly influence the deposition, distribution, retention, concentration and ultimate "uptake" of any applied chemical. According to Hoskins (1962), a pesticide deposit is defined as a coating either continuous or discrete, placed on the surface of a plant to kill or disable a pest, present or projected to arrive at a given time. Gunther and Blinn (1955) restricted that definition to an "effective deposit" which means that all but the material adhering to the plants surface sloughs off. This deposit then becomes a residue to be affected by weathering, metabolic alteration or other processes.

In order to overcome the surface irregularities causing water repellancy which prevent an intimate contact between a chemical and the cuticle, "surfactants" are added in various formulations to overcome any water repellancy (Crafts and Foy, 1962). Martin (1957) recovered DDT crystals from the surface of DDT treated leaves following solvent evaporation. However, when DDT was applied as an emulsion, very few crystals were recovered suggesting that the formulation had facilitated incorporation into the surface wax. According to Crafts and Foy (1962), the irregularities of the plant surface waxes alter the contact angle of the chemical and as a consequence the degree of surface wetting is determined

by 1) the nature of the functional group at the plant surface, 2) the degree of roughness, and 3) the presence or absence of an air film. Hoskins (1962) pointed out that the expansion of leaves and fruits also affects the total concentration per unit area by decreasing the density of the deposit with tissue growth.

Orgell (1954) and Schieferstein (1967) have suggested that a gradient from low polarity associated with the exterior of the plant cuticle, to a relatively high polarity within the layers of the epidermal cells, accounts for the variations they observed in the rates of movement across the cuticular barrier.

Although the cuticular layer is often viewed as a continuous layer over the surface of the above ground portions of plants, considerable evidence exists to demonstrate its wide variability, with respect to permeability. With age, the cuticle oxidizes, becoming less permable; however, associated with the aging is surface cracking, as a result of weathering or puncturing by insects, or areas where the wax is not evenly distributed, creating a physically imperfect layer which then permits increased penetration of both non-polar and polar chemicals (Crafts, 1956; 1961a; 1961b).

The environment is an equally important facet (Hull, 1970) in cuticle-chemical interaction. With herbicides, it has been shown that an increase in temperature is accompanied by a significant increase in uptake, although the response is affected by both the chemical and surface as well. Humidity is of great significance when considering interaction and uptake of organic and inorganic chemicals. High humidity favors stomatal opening and more importantly, slows the drying rate of the applied chemical, thereby extending the time for surface interaction. Another important

consideration is the decreased foliar hydration, which is also favored by this condition. With significant amounts of rain, however, leaching from the surface becomes an important consideration, since moisture can facilitate loss from the surface both to the atmosphere and soil. Hull pointed out that leaching increased with leaf maturity and concommitantly, became independent of light and other environmental parameters.

Some 15 years ago (Currier and Dybig,1960) suggested that the effect of light on insecticide permeability could not be assessed. This generality still remains true. There exist conflicting reports on the interactions at the cuticular surface. Hull reported that any chemical remaining on the surface of the leaf or fruit for any length of time may be photochemically altered. Since pesticides vary in their susceptability to photoalteration, penetration of any of the photoproducts might be hindered or facilitated by any molecular change of the parent compound.

Cuticular penetration has been theorized to involve three phases: 1) binding of the compound at the cuticle-spray interface (epicuticular wax), 2) the sorption of the molecule into the bulk of the cuticle either by absorption on the internal surface or solution within the cuticle, and 3) uptake of the chemical into the plasma membrane of the epidermal cell.

According to Bukovac (1974), differences of opinion exist as to the role of the hydrogen ion concentration on the penetration of foliar applied herbicides, and in order to fully assess its effect, one should separate the effects of pH on the penetrant from those on the plant. Orgell (1957) when studying non-inuried apricot leaf discs in the presence of polar solutes in aqueous solution, e.g. acids bases, salts, dyes, etc., reported the absence of detectable penetrating substances, even after 48 hr of exposure. He reported that the pH of the solution and the type of surfactant were the major factors affecting sorption of acetic or

basic substances. The sorption of acidic compounds increased with decreasing pH, whereas the sorption of basic compounds increased with increased pH. Apparently, the repression of the dissociation causes the applied chemical to penetrate more readily (naturally due to its more lipophilic nature).

Although the exact penetration pathway is not known, it appears that there exists both a non-polar and a polar route of cuticular entry. Data suggest that hydrophobic compounds will follow the non-polar route and hydrophilic compounds associate with the polar route of uptake. According to Ebeling (1964), the speed of surface association and ultimate penetration of non-polar compounds is quite fast. Bukovac (1976) stated that the diffusion into and through the cuticle is the most likely mode of herbicide entry and that the concentration is a direct function of the contact time and area, both of which are a reflection of the degree of surface wetting.

EXPERIMENTAL

Reagents

a. Heptachlor (Applied Science Labs. Inc.) 99% pure; used as received.

b. Benzophenone (J.T. Baker Chemical Co.) following g.l.c. analysis was was used without further purification.

c. Undecane ($C_{11}H_{24}$) (Columbia Organic Chemicals) Purification was carried out by repeated washings with sulfuric acid until there was no yellow color left. $KMNO_4$ was added to further oxidize any residual contaminates. The solution was then distilled *in vacuo* and the third cut was taken and used for experimentation.

d. n-Decanol ($C_{10}H_{22}O_1$) (Dupont; Polychemicals Dept.) Purification was by vacuum distillation and the middle fraction was used for experimentation.

e. Octacosane ($C_{28}H_{58}$) (Aldrich Chemical Company, Inc.) was used as received.

f. Ceryl Alcohol ($C_{26}H_{54}O_1$) (INC Pharmaceuticals, Inc.) was used as received.

g. 14-Heptacosanone ($C_{27}H_{54}O_1$) (INC Pharmaceuticals, Inc.) was used as received.

h. Carbonyl fraction (compliments of Milica Milosaljevic, Phd.) was obtained by column chromatography of the surface waxes of tomato, *Lycopersicon esculentum*.

Solvents

a. Hexane (Mallinckrodt Chemical Works) Nanograde; used as received.

b. Acetone (Mallinckrodt Chemical Works) Nanograde; used as received.

c. Benzene (Mallinckrodt Chemical Works) Spectophotometric Grade; used as received.

Equipment

Irradiation.

a. All samples were irradiated in a photochemical reactor (Rayonet Photochemical Reactor; Southern N.E. Ultraviolet Co.). The source was fitted with RUL 3000 lamps, having a peak energy output of 90% at 300 n (Fig. I).

b. Solution Photolysis; sample tubes were hung from a cross bar fixed to the top of the photochemical apparatus and adjusted to the center of the light source.

c. Film Photolysis; sample Pyrex petri dishes were mounted to the surface of a glass thin layer chromatography plate which had been fixed to the surface of a carousel or were set on the surface of a crystallizing dish, filled with sand and adjusted to the desired temperature by a Corning laboratory hot plate.

Analytical Instruments

All analyses for photoproducts were made on the following gas liquid chromatography (g.l.c.) instruments equipped with flame ionization detectors:

GLC - 1 Beckman, model GC-4 with Bristol Dynamaster recorder and disc integrator, Model 202.

GLC - 2 Beckman GC-65 with Beckman recorder

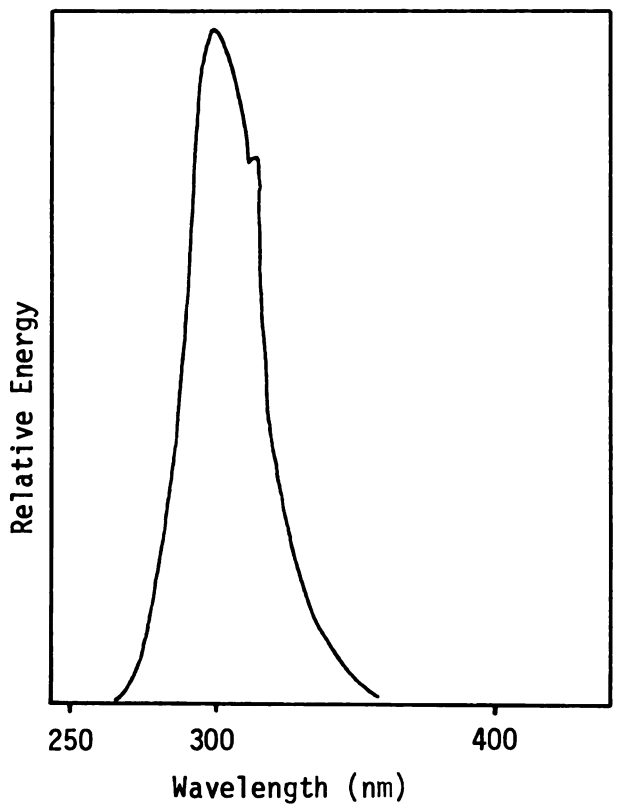


Figure 1. Energy output distribution of RUL 3000 UV lamps.

GLC - 3 LKB 9000 gas chromatograph

GLC - 4 Varian 2740 gas chromatograph

Several g.l.c. columns (COL) were utilized throughout the investigation in order to confirm results.

COL 1- 6'x1/8" glass column containing 3% SE-30 on 80/100 mesh Gas Chrom Q.

COL 2- 6'x1/8" glass column containing 3% OV-17 on 80/100 mesh Gas Chrom Q.

COL 3- 6'x1/8" glass column containing 1% OV-1 on 100/120 mesh Gas Chrom Z.

COL 4- 2'x1/8" glass column containing 3% Dexil 300 on 100/120 mesh Gas Chrom W.

COL 5- 6'x1/8" glass column containing 2% OV-1 on 100/120 mesh Gas Chrom Z.

COL 6- 1'x1/8" glass column containing 2% OV-1 on 100/120 mesh on Gas Chrom Z.

All g.l.c. analyses were carried out using the following instrumental settings: 140°---340°, at 2.5°/minute; 30 ml flow rate at .2"/minute recorder speed.

Mass spectral data were obtained from a Dupont 21-490 mass spectrometer, interfaced via a jet separator with GLC-2 (COL 1-6), or with a direct probe, and interfaced to a PDP-12 LDP computer operating under MASH software. Mass spectral data were also gathered from the L.K.B., Model 9000 Mass Spectrometer, equipped with a mass marker and a gas chromatograpic inlet; it is interfaced to a PDP-8e computer system (SYSTEMS INDUSTRIES).

EXPERIMENTAL PROCEDURES

Sample Preparation

Class A volumetric flasks and pipettes were used exclusively to prepare all photolysis solutions, films and reference standards.

Stock solutions of heptachlor and other standards were prepared in 25 ml volumetric flasks, with the stock solutions at a concentration of 1000 ppm (ug/ml).

All control experiments were carried out in the dark, in triplicate.

Experiment 1.

Heptachlor crystals (0.185 mg) were dissolved in 20 ml of n-hexane, from which a 5 ml aliquot was pipetted onto the bottom of a 5 cm Pyrex petri dish. The solvent was vacuum evaporated and the film photolyzed for 24 hours, without a cover plate.

Experiment 2.

The previous experiment was repeated except that the cover plate was placed over the petri dish in order to cut off the light energy below 290 nm. Photolysis was carried out for 24 hr.

Experiment 3.

Heptachlor (18.5 mg) was dissolved in 20 ml of n-hexane. A 10 ml aliquot was pipetted into a quartz reaction vessel. The solution was rotated continuously to facilitate evaporation as well as to obtain a relatively even coating on the inner surface of the vessel. It was sealed with a ground glass stopper and mounted on a metal frame. The apparatus was then placed on the roof of the Pesticide Research Center and remained there from June 10, 1972 to September 10, 1972. This experiment was repeated the following year from June 6, 1973 to September 30, 1973.

Experiment 4.

Epicuticular wax was isolated from mature tomato fruit (Lycopersicon esculentum), by 3, 3 second dips of the fruit in chloroform. The total solvent extract was pooled, transferred to a large round bottom flask and the chloroform removed on a Buchner rotating vacuum evaporator and the residue taken up in 10 ml benzene. A 5 ml aliquot was in turn pipetted from this stock solution onto the bottom of a Pyrex petri dish, and the solvent vaccum evaporated. Just prior to the complete evaporation, leaving only the was film, 37.0 mg of finely powdered heptachlor was added to the surface of the wax and the evaporation was completed. This preparation was photolyzed for 24 hr.

Experiment 5.

Following the clean-up and purification of the undecane, 2 ml of this standard was combined with 37.0 mg of heptachlor and 0.2 ml of acetone, which served as a sensitizer. The solution vials were sealed and photolyzed from 0 to 24 hr. Photoproducts were formed within 5 hr and no additional products were formed after 24 hr of photolysis.

Experiment 6.

The same arrangement was followed for the solution photolysis of n-decanol as described in Experiment 5.

Experiment 7.

Octacosane (39.4 mg) (0.05M) standard was prepared in 20 ml benzene. Heptachlor (37.0 mg) was prepared in 20 ml benzene. One ml each of the alkane, Heptachlor and 0.2 ml of acetone were pipetted into Pyrex screw cap vials. The solution was photolyzed from 0 to 3 days.

Experiment 8.

The same experimental procedure was carried out during this experiment as described for Experiment 7.

Experiment 9.

The same concentrations of the alcohol to heptachlor were prepared as described in Experiment 7 and the same experimental set-up was used except that the photolytic period was extended to 5 days.

Experiment 10.

In order to examine the sensitizing capacity of the carbonyl fraction isolated from tomato cuticular waxes, a 1 ml aliquot each of Heptachlor and 14-Heptacosanone (0.05M) were combined with 0.2 ml of the carbonyl solution and placed in a Pyrex screw cap vial. All standards were prepared in benzene. A 2 ml aliquot of this solution was then photolyzed for 5 days; samples were taken daily and analyzed on the gas chromatograph until there was no change in the elution profile. An aliquot of this 5 day photolysis solution was then photolyzed for an additional 5 days.

Experiment 11.

The same experimental procedure was carried out as described above except that octacosane (C_{28}) (0.05M) was used in place of the ketone. Its initial photolysis period was 5 days and then extended for an additional 5 days.

Experiment 12.

In order to approach the platelet morphology of the surface waxes of pear leaves, which has been described as being high in ketone concentration, 26.6 mg of 14-Heptacosanone was weighed out, dissolved in 2 ml benzene pipetted onto the bottom of a Pyrex petri dish and the solvent

evaporated under vacuum. One ml of a 4000 ppm standard of Heptachlor was applied to the surface of the dried wax, the solvent evaporated and a cover plate placed over the dish. This was then placed on the surface of a crystallizing dish, which had been filled with sand and equilibrated at a temperature of 70°, just under the melting point of the ketone (73°C). This film was photolyzed for 5 days.

Experiment 13.

The same experimental procedure carried out in Experiment 12 was repeated, except that Octacosane (C_{28}) was used in place of the ketone. This particular chain length was selected because it represented a carbon length common to the surface waxes of the tomato fruit cuticle.

Experiment 14.

The same experimental procedure was followed as above, however, 0.1 ml of the carbonyl solution was added to the hydrocarbon prior to evaporation, to serve as a "natural" sensitizer.

Experiment 15.

The same procedure as reported in Experiment 14 was followed throughout this experiment except 24.2 mg benzophenone was used in place of the carbonyl fraction, as an artificial sensitizer.

Experiment 16.

Thin layer chromatography (tlc) of the "naturally derived carbonyl fraction" showed that it contained minute amounts of fatty acids, esters, aldehydes, and ketones. There was also a large quantity of an unknown which was shown to be various alcohols by comparisons to standard Rf's.

RESULTS

Heptachlor is a white crystalline solid, melting betweein 96-98°C. The mass spectrum (Figure 1) of heptachlor shows $M^{+\cdot}$ at m/e 370 and a series of characteristic ion fragments at m/e 335 ($M^{+\cdot}$ -1 Cl), m/e 300 ($M^{+\cdot}$ -2 Cl) m/e 265 ($M^{+\cdot}$ -3 Cl) and 100 ($M^{+\cdot}$ -6 Cl).

Film photolysis of heptachlor for 24 hr yielded four photoproducts and their isomers (Figure 2). The two photodechlorinated isomers, 1.4.6.7.8.8-hexachloro-3a,4,7,7a tetrahydro-4,7- methanoindene (II) and 1,4,6,7,8,8-hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (III) were identified as the first compounds to elute from column 1. The mass spectrum showed a series of prominent ions at m/e 335 ($C_{10}H_5Cl_6^+$), m/e 300 ($C_{10}H_5CL_5^+$), m/e 265 ($C_{10}H_5CL_4^+$) and m/e 100 ($C_5H_5Cl_1^+$). The third identified was heptachlor epoxide (VI) with diagnostic fragments at m/e 386 ($C_{10}H_5Cl_7O_1^+$), and m/e 350 ($C_{10}H_5Cl_6O_1^+$) which represents the loss of a chlorine atom. The fourth compound identified was an HCl adduct to heptachlor (VII). These photoproducts were identified from a hexane washing of the petri dish. However, there appeared to be a hexane insoluble residue which was removed by washing with acetone. When this residue was analyzed it was found to contain all of the compounds described above plus an oxygen analogue which is believed to be either a di-epoxide (VIII) or an epoxide-ketone (IX) form of heptachlor. The subsequent photochemical experiment with the Pyrex petri dish cover plate on for 24 hr, revealed the presence of only one photoproduct,

Figure 1. Mass spectrum of heptachlor.

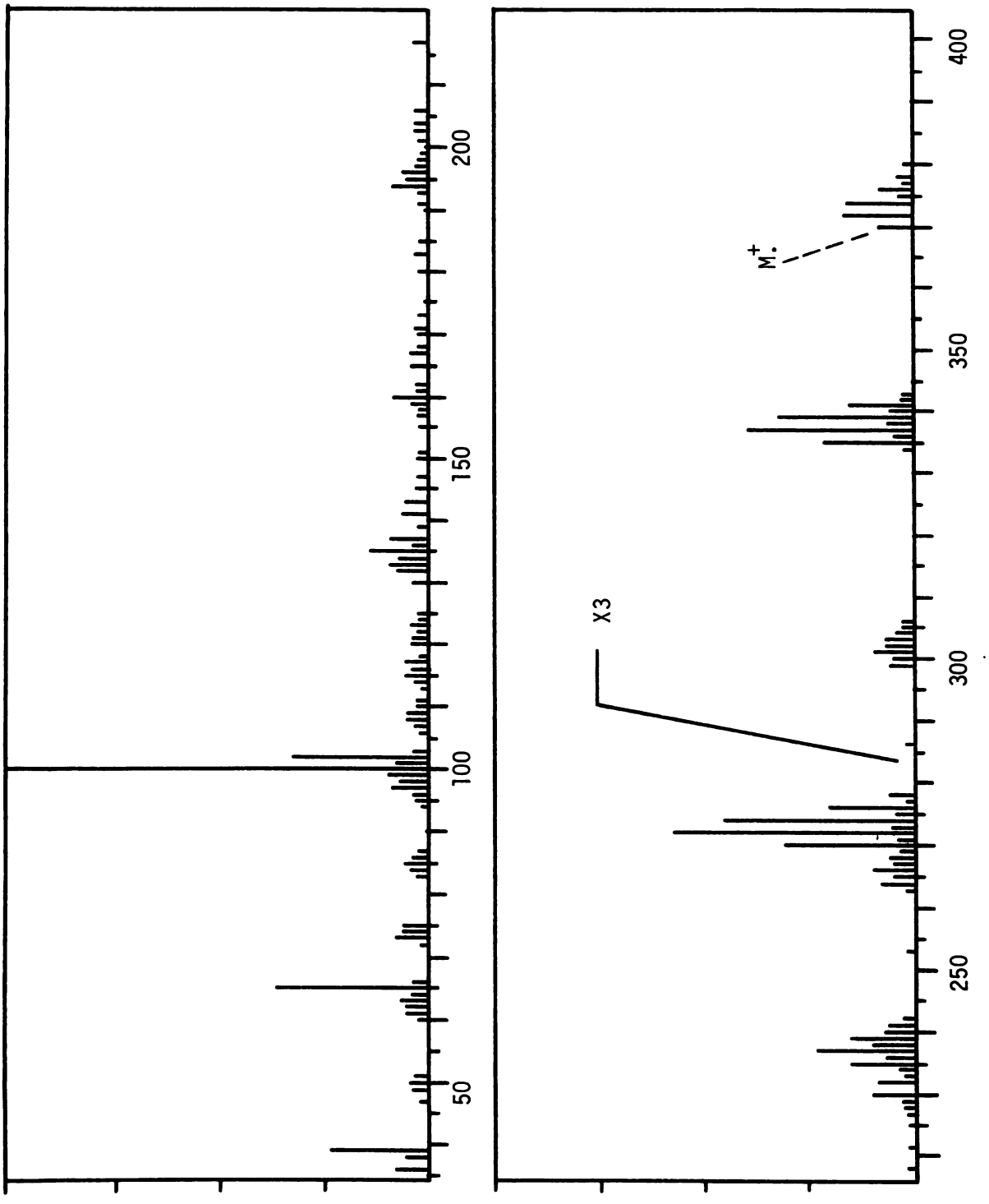
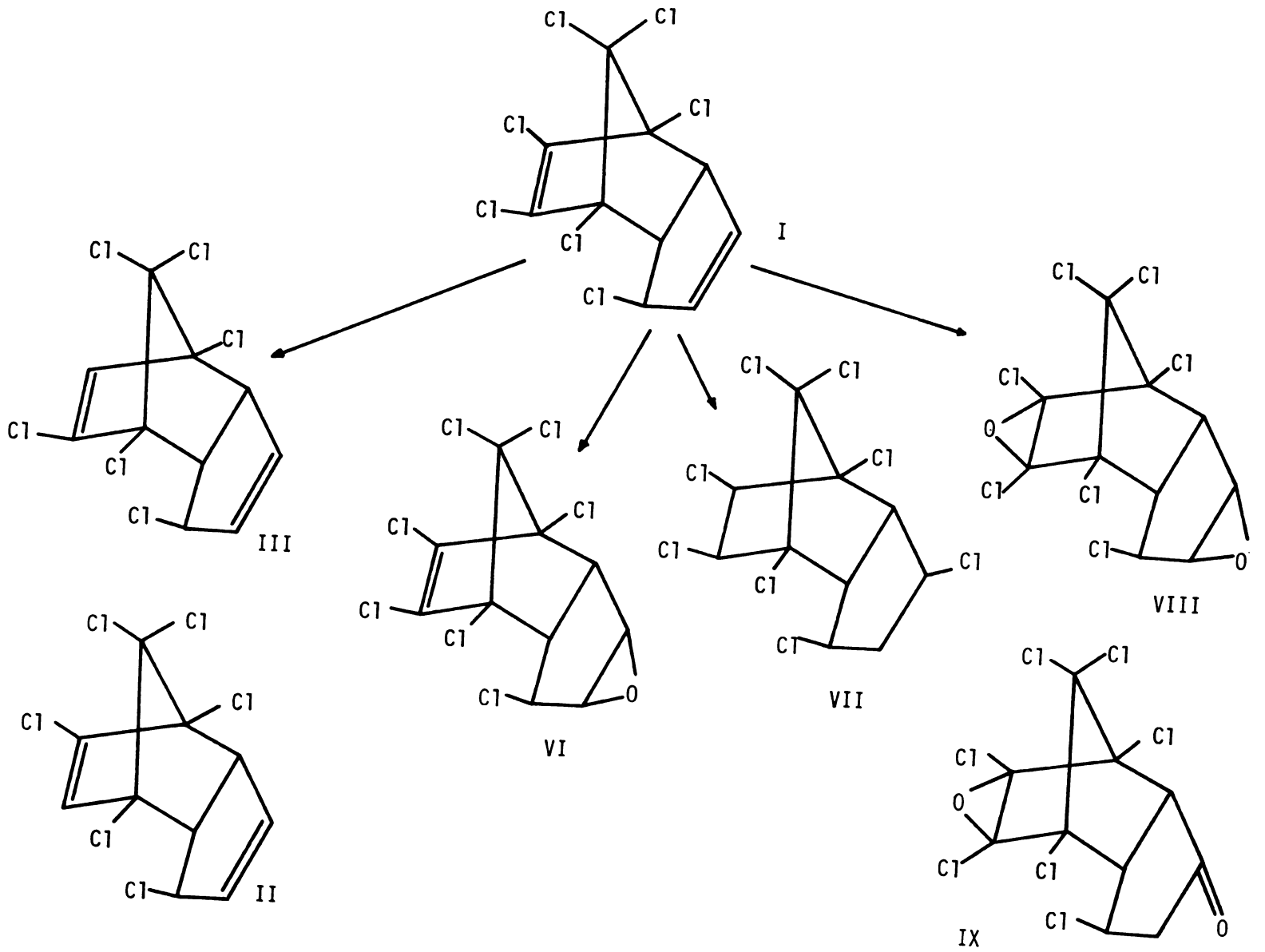

50
100
150
200
250
300
350
400
X3
M+.

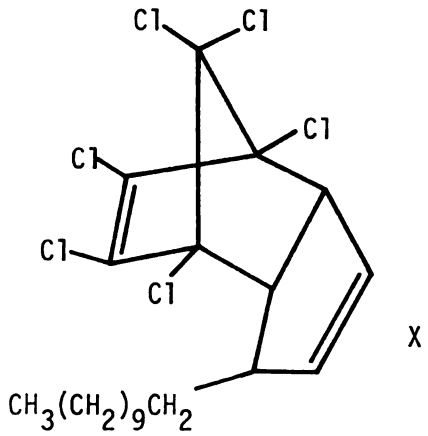
Figure 2. Photoproducts of the 24 hour film photolysis of heptachlor.


Cl
O
I
II
III
VI
VII
VIII
IX

heptachlor epoxide.(VI). Following three additional days of photolysis however, the dechlorinated isomers (II) and (III) were also formed.

The photolysis of a heptachlor film in a quartz reaction vessel under sunlight yielded one photoproduct, the cage form of heptachlor (Table 2; IV), (2,3,4,4,5,6,10 heptachlor pentacyclo [5.3.0.$0^{2,6}$.$0^{3,4}$.$0^{5,8}$. decane]) in 10% yield. Its melting point was reported by Flotard (1968) to be 118-119°C. The melting point for heptachlor is 96-98°C. Although its mass spectral fragmentation is very similar to heptachlor, it elutes after heptachlor, on all experimental g.l.c. columns.

Photolysis of an epicuticular wax film in the presence of heptachlor produced only one photoproduct the cage form of heptachlor (IV). This conversion strongly suggests the presence of natural sensitizers

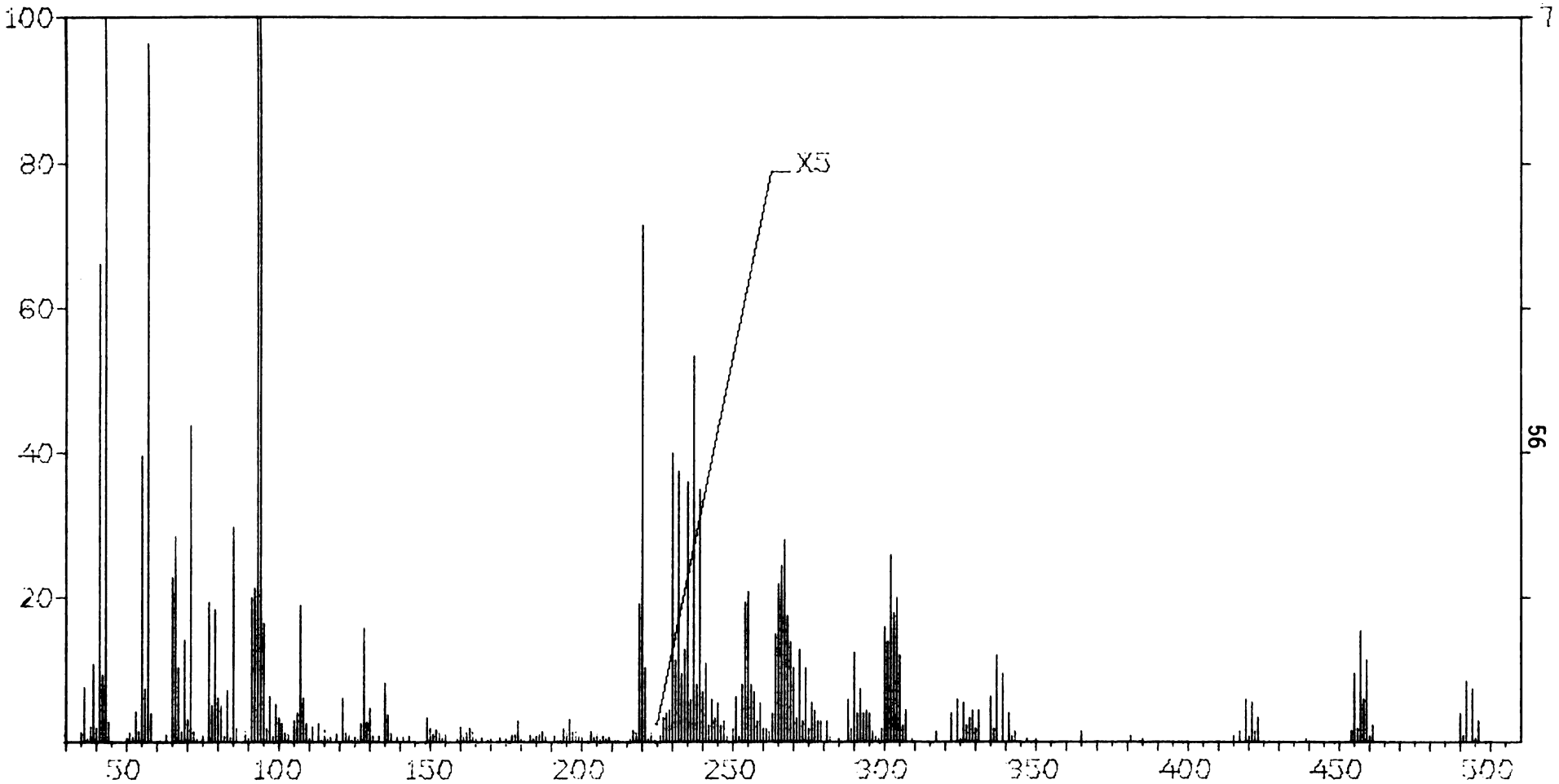


X

in the wax.

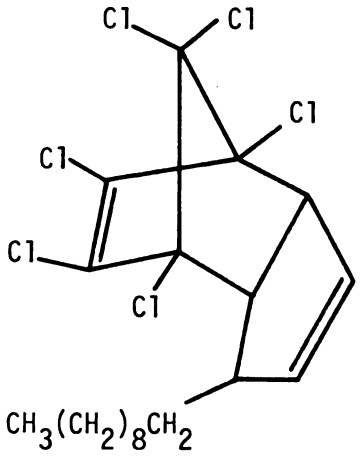
The photoproducts formed following the photolysis of undecane, heptachlor and acetone produced the following compounds: the dechlorinated isomers (11) and (111) and 4 isomers of the solvent adduct of heptachlor attached to the C_1 position of the cyclopentene ring of the heptachlor molecule (X). The mass spectrum of these isomers (Figure 3) showed a parent ion m/e 490 ($C_{21}H_{28}Cl_6^+$), with the next distinct fragment at m/e 455 ($C_{21}H_{28}Cl_5^+$), indicating the loss of a chlorine atom,

Figure 3. Mass spectrum of one of the photoisomers resulting from 24 hour photolysis of undecane and heptachlor, in the presence of acetone as a sensitizer.


100
80
60
40
20
X5
50
100
150
200
250
300
350
400
450
500

followed by the next most intense ion at 335 ($C_{10}H_5Cl_4^+$). Although these were the basic fragments, there was some variation between the pattern of the isomers and no attempt was made to determine the individual stereochemistry of each isomer.

Analysis of the solution photoproducts of n-decanol, in the presence of heptachlor and acetone resulted in the addition to C_1 of the solvent molecule, as described in the previous experiment (XI). Its



XI

molecular ion M^+ was at m/e 475 ($C_{20}H_{25}Cl_6^+$). followed by the next more intense fragment at m/e 335 ($C_{10}H_5Cl_6^+$) and m/e 140 ($C_{10}H_{20}^+$); since the molecular weight of the alcohol is 158 and the latter intense peak was m/3 140, the difference of 18 indicated the loss of H_2O from the alcohol molecule.

Photolysis of octacosane ($CH_3(CH_2)_{26}CH_3$), heptachlor and acetone for 24 hours resulted in the following photoproducts; hexachlor isomers II and III, in 38% yield, an olefinic form of the alkane as a minor product and a pair of unresolved hexachlor dimers, in 36.9% yield. Figure 4 shows the g.l.c. elution profile of this mixture. At 175° the dechlorinated isomers elute as an unresolved peak. However, with repetitive scanning on the mass spectrometer the spectra of two compounds could be

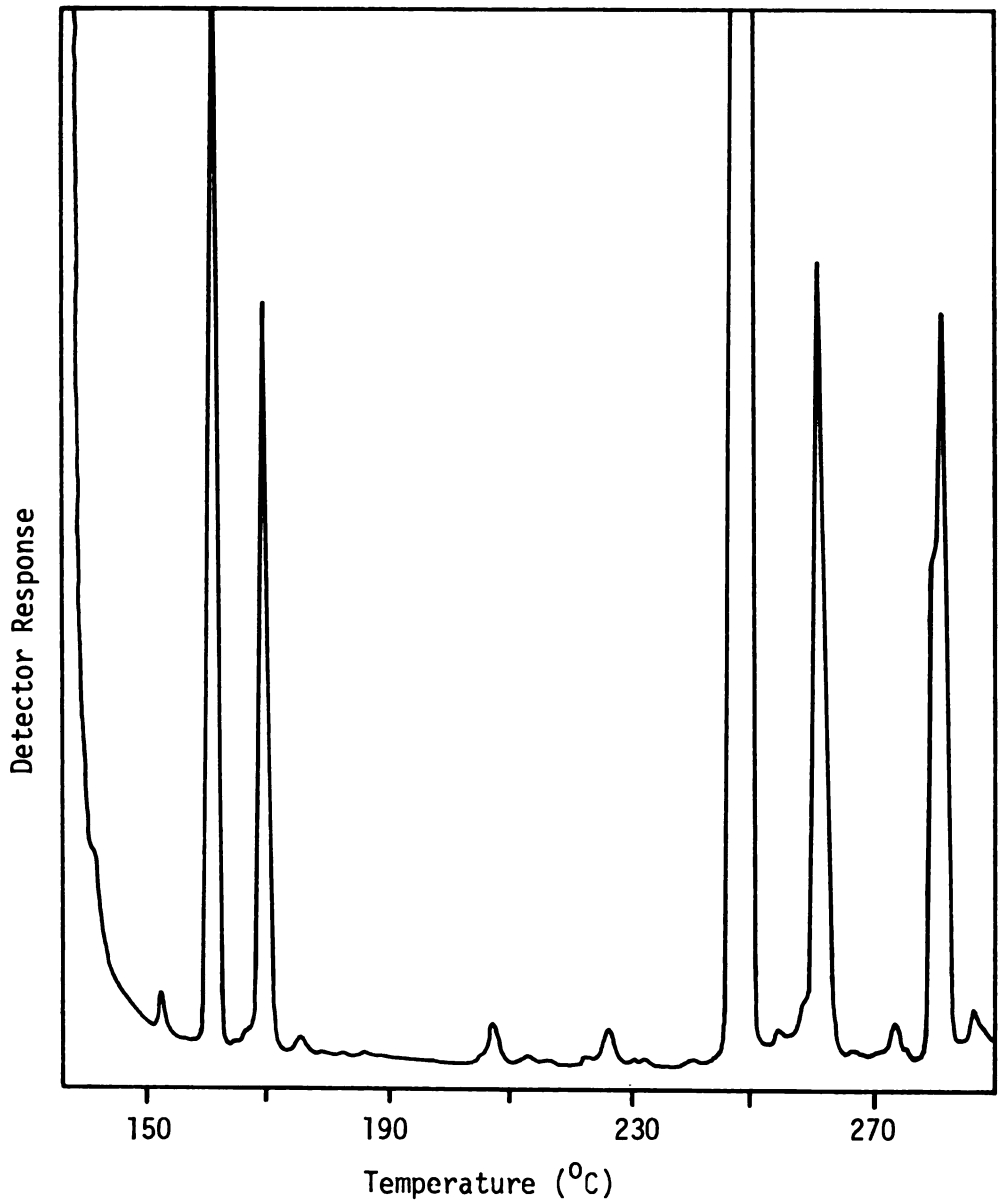
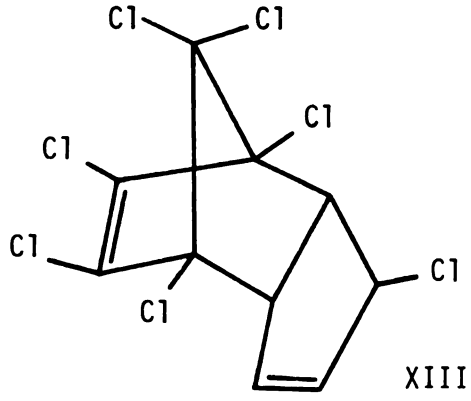


Figure 4. G.L.C. profile of photoproducts on Varian 2740 resulting from 24 hour photolysis of octacosane, heptachlor and acetone (Varian 2740 Gas Chromatograph).

obtained. The unreacted alkane eluted at 250°, followed by the olefin, at 260°. At 275° the pair of dimers eluted. Figure 5 shows the mass spectrum of one of the dimers. In Figure 6 the possible stereoisomers are presented; however, since there was insufficient material, an exact structural determination of each isomer was not possible.

The solution photolysis (Experiment 9) of 14-Heptacosanone, heptachlor and acetone for 24 hr resulted in a similar series of photoproducts. The g.l.c. profile, Figure 7 shows that under the same experimental conditions the photoisomer II and III were formed in 38% yield; but more important was the formation of two pairs of hexachlor dimers, each pair being well resolved and separated. Collectively the two pairs



XIII

of dimers were formed in 25.1% yield; the mass spectrum for both pairs was the same shown presented in Figure 5. It was necessary that all of the components of the photolysis mixture be present in both of the previous two solution experiments (8 and 9); if any one component was absent no photoproducts were formed (Table 1).

Analysis of the ceryl alcohol-heptachlor photolysis mixture (Experiment 8) showed the following results: there appeared on the g.l.c. profile a slight resolution of the isomer of unreacted heptachlor (XIII). This was followed by the hexachlor isomer 11 and 111, as reported in the previous experiments. The important finding of this experiment was

Table 1. The Requirement of the sensitizer, acetone, for photoproduct formation

	Compound	Solvent	Pesticide	Sensitizer	Results
Experiment 7					
C_{28}	Alkane	Benzene	Heptachlor	Acetone	
1	+	+	-	-	-
2	+	+	+	-	-
3	-	+	+	+	-
4	+	+	+	-	-
5	+	+	+	+	+
Experiment 8					
C_{27}	Ketone	Benzene	Heptachlor	Acetone	
1	+	+	-	-	-
2	+	+	+	-	-
3	-	+	+	+	-
4	+	+	-	-	-
5	+	+	+	+	+
Experiment 9					
C_{26}	Pri. OH	Benzene	Heptachlor	Acetone	
1	+	+	-	-	-
2	+	+	+	-	-
3	-	+	+	+	-
4	+	+	+	-	-
5	+	+	+	+	+

Figure 5. Mass spectrum of one of the several hexachlordimers formed during the 24 hour photolysis of heptachlor, octacosane and acetone in benzene.

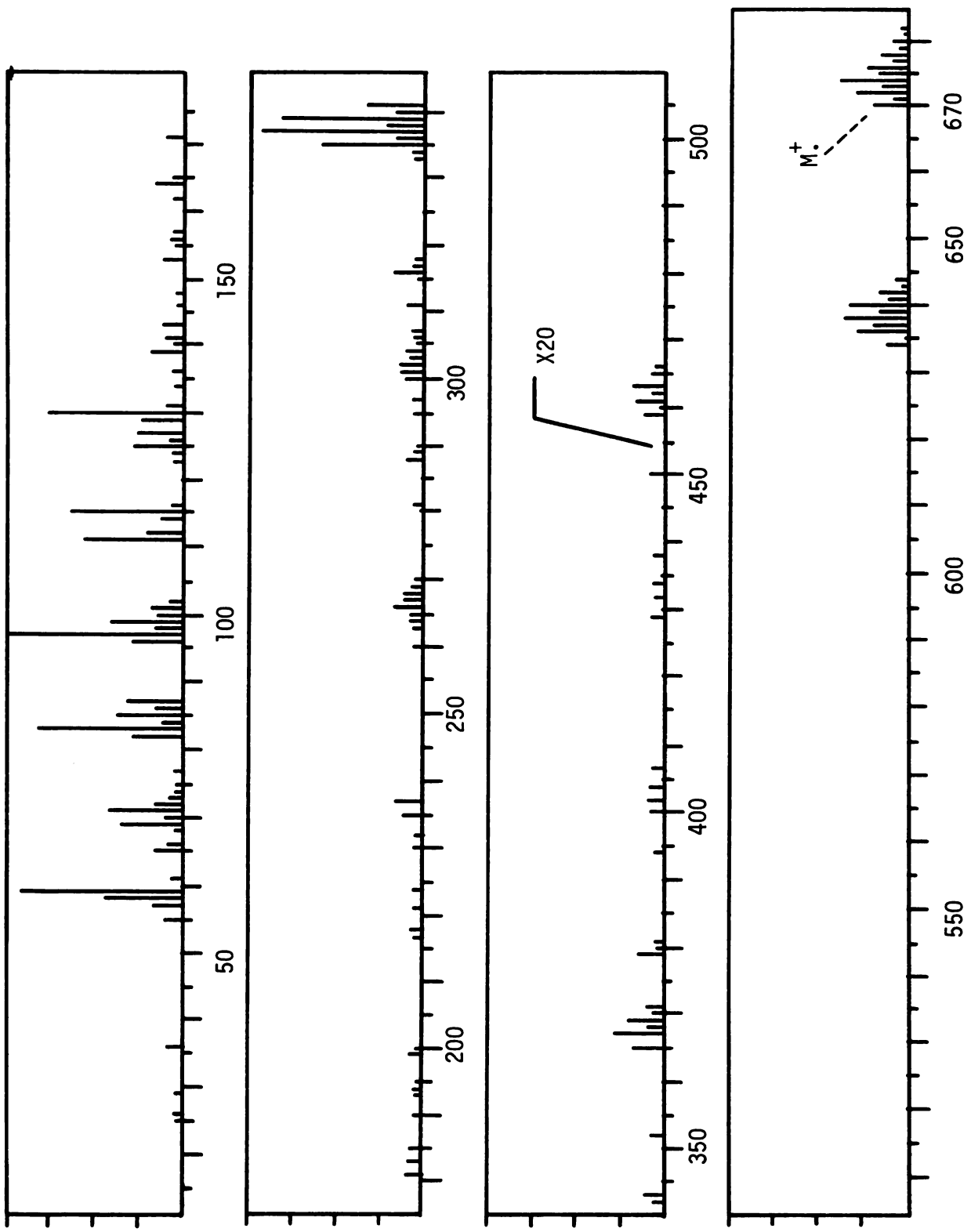
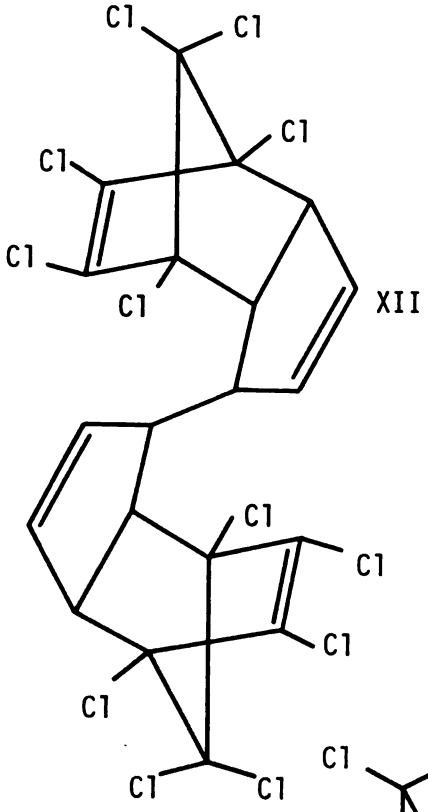
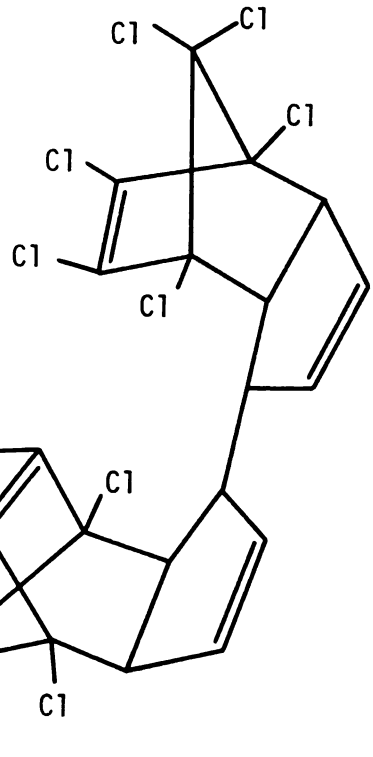

50
100
150
200
250
300
350
400
450
500
550
600
650
670
X20
M+.

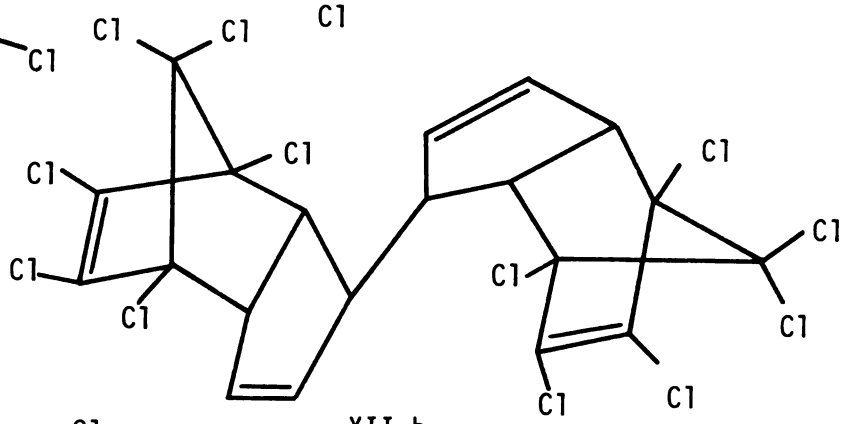
Figure 6. Suggested structures of the stereoisomers of the hexachlor dimers.



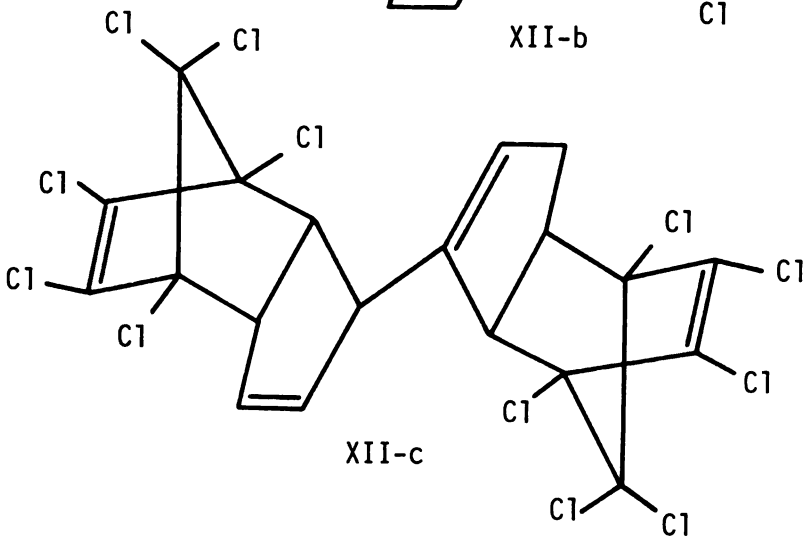
XII



XII-a

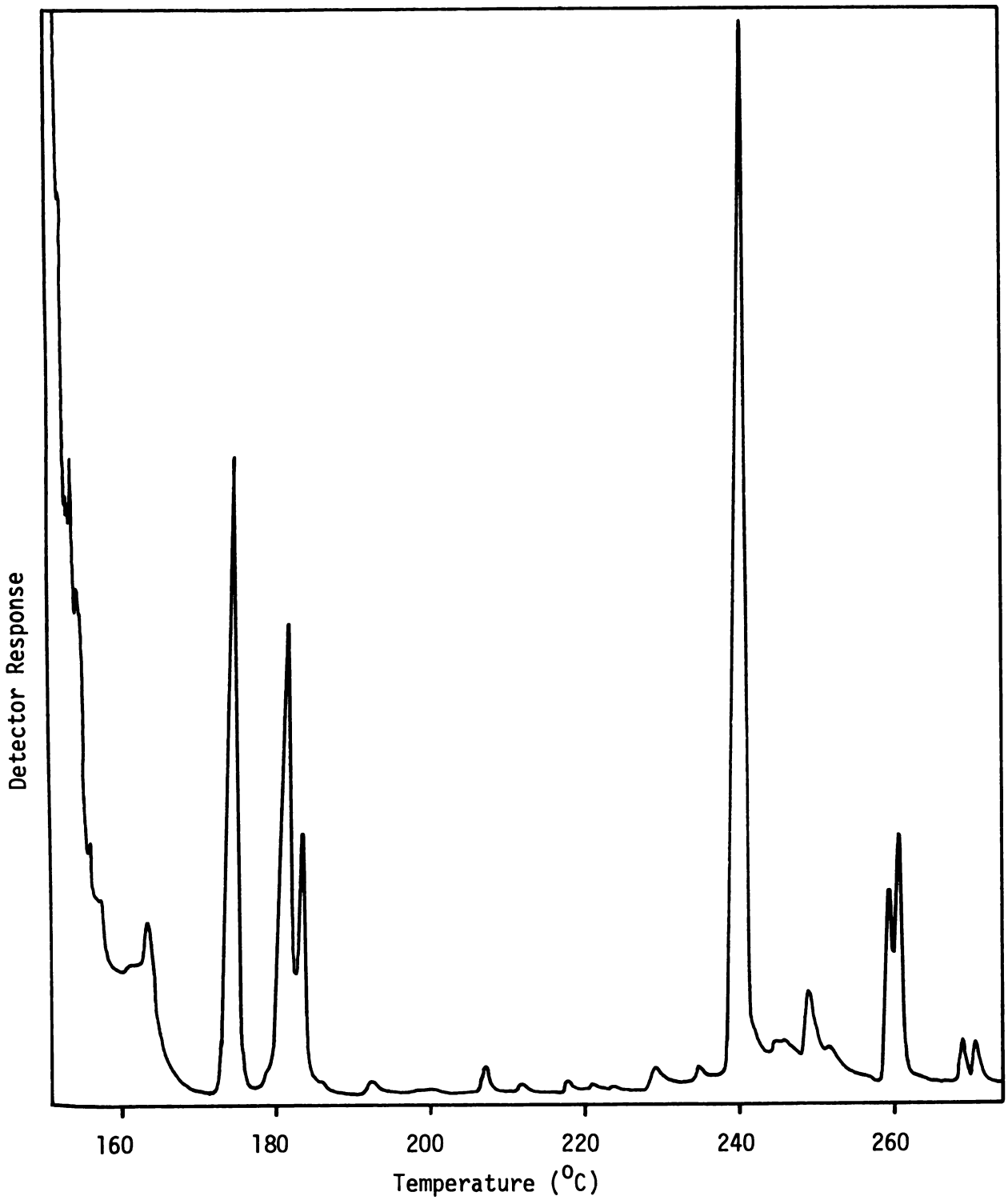


XII-b



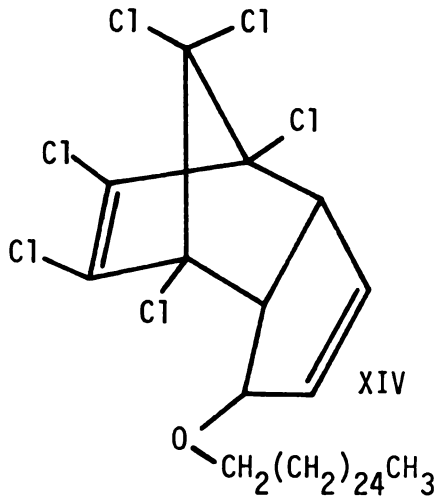
XII-c

Figure 7. The G.L.C. elution profile of the photoproducts resulting from the 24 hour photolysis of 14-heptacosanone, heptachlor and acetone (Beckman 65 Gas Chromatograph).

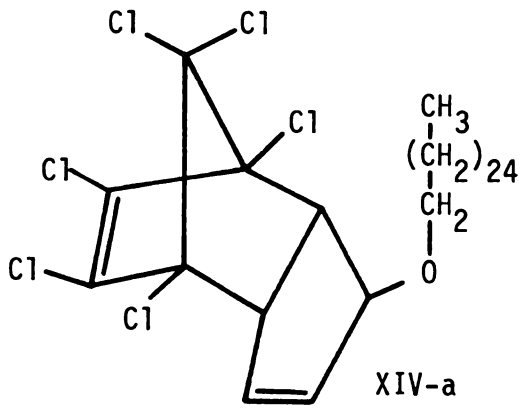

Detector Response
160
180
200
220
240
260
Temperature (°C)

a pair of additional isomers between hexachlor and ceryl alcohol. Detailed analysis of these two compounds showed there to be some ambiguity in the structural interpretation and therefore both interpretations should be presented (Table 2).

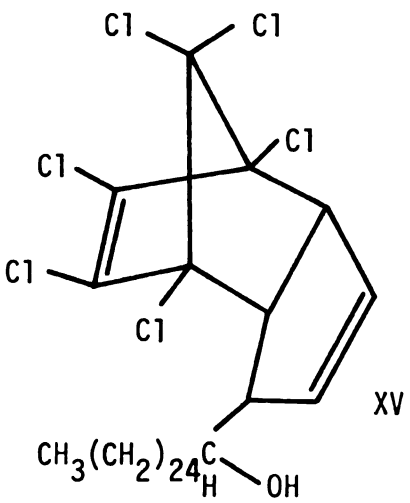
The assumption was made that a straight addition occurred between the ceryl alcohol and hexachlor. Linkage could, however, occur as O-$(CH_2)_{25}CH_3$ resulting in an ether linkage: alternatively, the hexachlor radical could attack the alpha methylene group of the alcohol resulting in a C-C linkage. The addition of the alcohol to the hexachlor radical



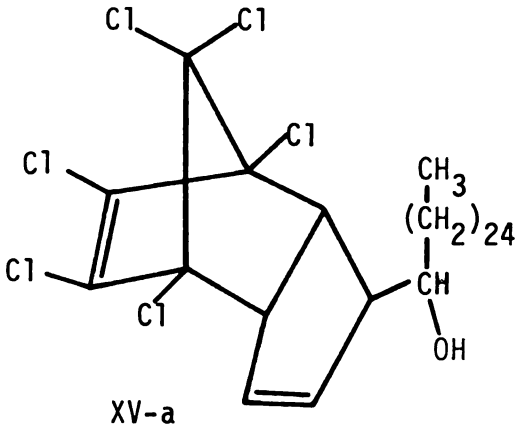
XIV



XIV-a



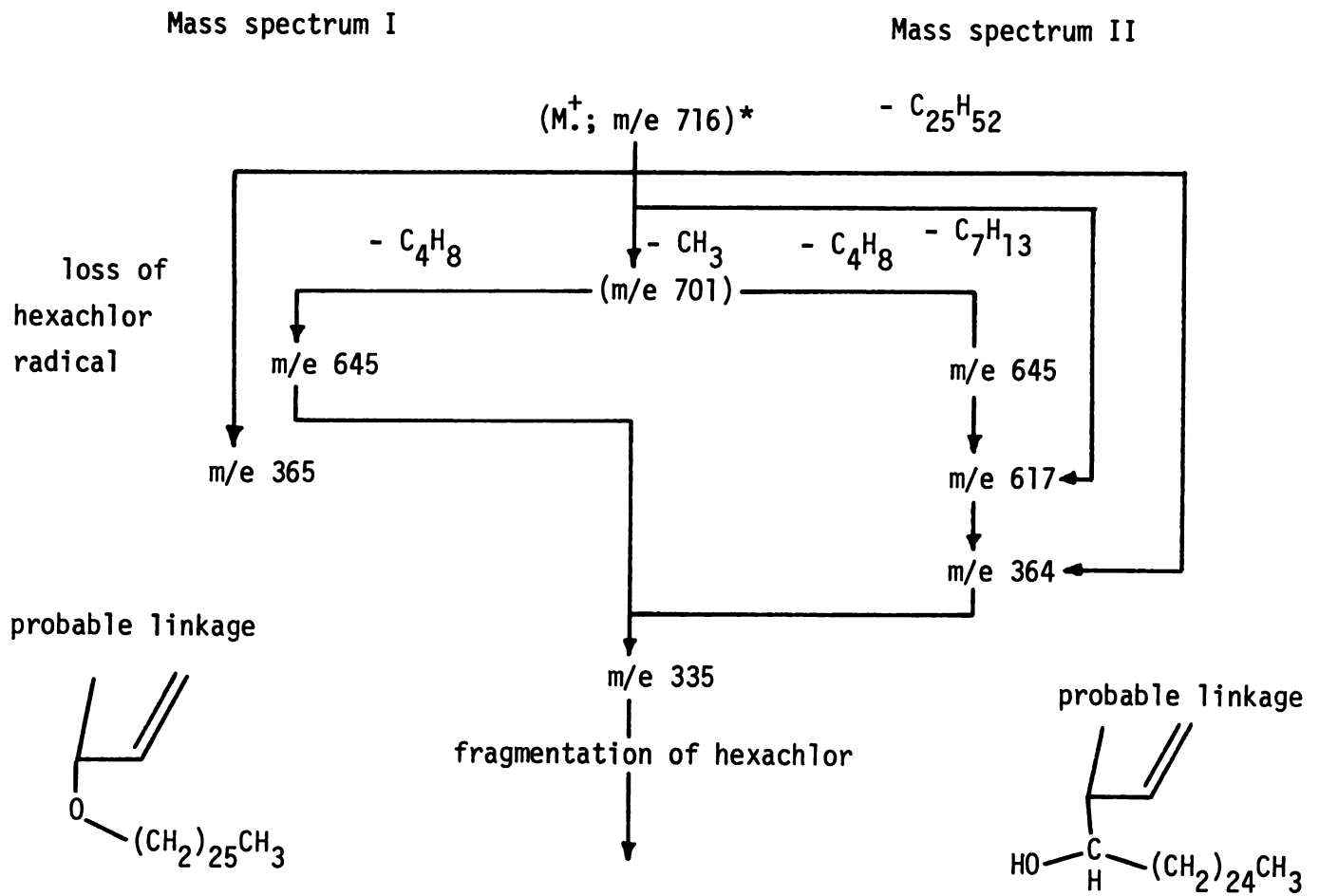
XV



XV-a

would result in a molecular weight of M^+ 716, which was not observed; the first fragment seen is m/e 647. This can be explained by the

Table 2. Fragmentation pathways of the photolytic adducts of ceryl alcohol and hexachlor.



* ( ) = no ion found

elimination of an alkyl fragment from $M^{+\cdot}$ 716 (not present) via first the loss of $\cdot CH_3$, leading to m/e 701 (not present) and this is followed by the successive loss of CH_2 units to m/e 647, which shows the first chlorinated fragment. This is followed by an intense fragment at m/e 335, ($H_{10}H_5Cl_6^+$) - hexachlor.

The photoproducts from 5 day photolysis of both Experiments 10 and 11 in the presence of the "carbonyl fraction" as the sensitizer, resulted in the formation of compounds II and III. The g.l.c. profile also showed again, a slight resolution of the other isomeric form of heptachlor (XIII).

To examine further any possibility of the sensitizing capacity of the ketone, an aliquot of the 5 day photolysis solution was photolyzed for an additional 5 days and then analyzed by g.l.c. and combined g.l.c.-m.s. The results were the same as reported above except at the higher g.l.c. temperature range. One pair of hexachlor dimers (1.5% yield) at the same temperature observed in the alkane - acetone sensitized experiment. The mass spectra were obtained at 25 eV since the amount of dimer formed was small and the compound is quite labile.

The 5 day photolysis of the 14-Heptacosanone - heptachlor film (Experiment 12) produced no detectable photoproducts. The same results were obtained when octacosane and heptachlor (Experiment 13) were combined and photolyzed for the same period of time.

The film photolysis of octacosane and heptachlor, in combination with the carbonyl fraction resulted in the formation of compounds II and III, as confirmed by combined g.l.c.-m.s.

The 5 day photolysis of octacosane, heptachlor and benzophenone (Experiment 15) resulted in a series of interesting benzophenone related

Figure 8. Benzophenone related photoproducts following 5 day film photolysis of octacosane, heptachlor and benzophenone.

photoproducts and heptachlor photoproducts (Figure 8). Acetophenone was identified as the first compound with the parent ion m/e 198 ($C_{14}H_{14}O_1^+$) and m/e 183 ($C_{13}H_{10}O_1^+$), m/e 105 ($C_7H_5O_1^+$), and m/e 77 ($C_6H_5^+$). This was followed by a chlorinated benzophenone; its parent ion m/e 216 ($C_{13}H_9O_1Cl_1^+$) and is followed by the same fragmentation pattern cited above. A benzyl-benzophenone was also formed with its parent ion m/e 258 ($C_{19}H_{14}O_1^+$) followed by an intense peak at m/e 182, the benzyl adduct to one of the benzene rings of benzophenone. Its remaining fragmentation pattern was the same as that for standard benzophenone. Unreacted heptachlor was present as well as the hexachlor isomers II and III of heptachlor.

Analysis of the carbonyl fraction following 5 days of photolysis showed no change in its gas chromatographic profile. When analyzed by combined g.l.c.-m.s., it showed a very high concentration of di-octyl phtalate. The fragmentation pattern for di-octyl phtalate gives peaks at m/e 279 and m/e 149. Its parent ion m/3 390 is generally never observed (Figure 9). Its absorption spectrum (Figure 10) shows absorption below 300 nm with peaks at 282 nm, 275 nm, and a strong peak at 223 nm. At a 100 times as was used in the experiments higher concentration it could feasibly act as a sensitizer for the inter-system crossing in the experiments where results were observed.

Figure 9. Mass spectrum of di-octylphthalate.

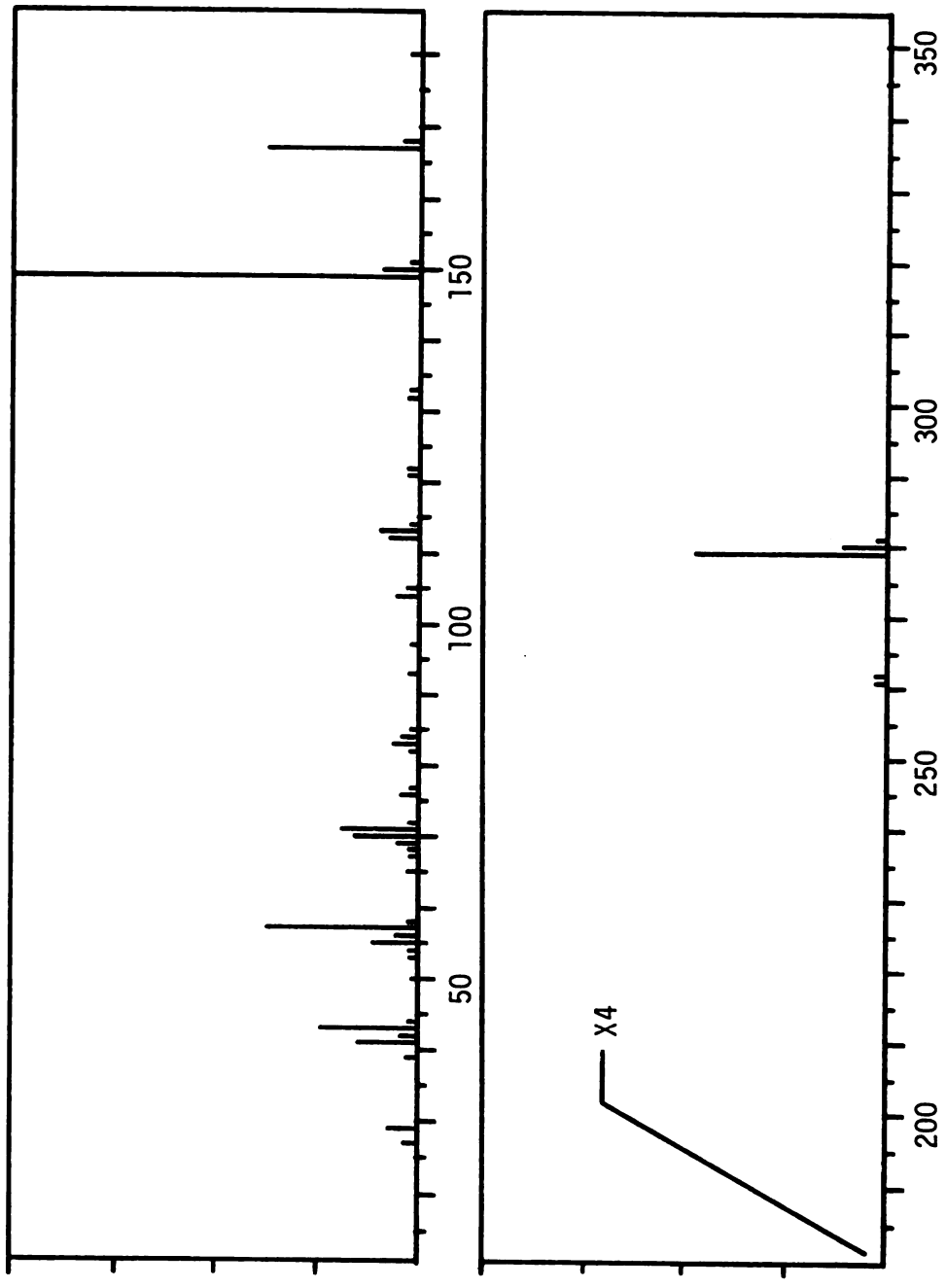
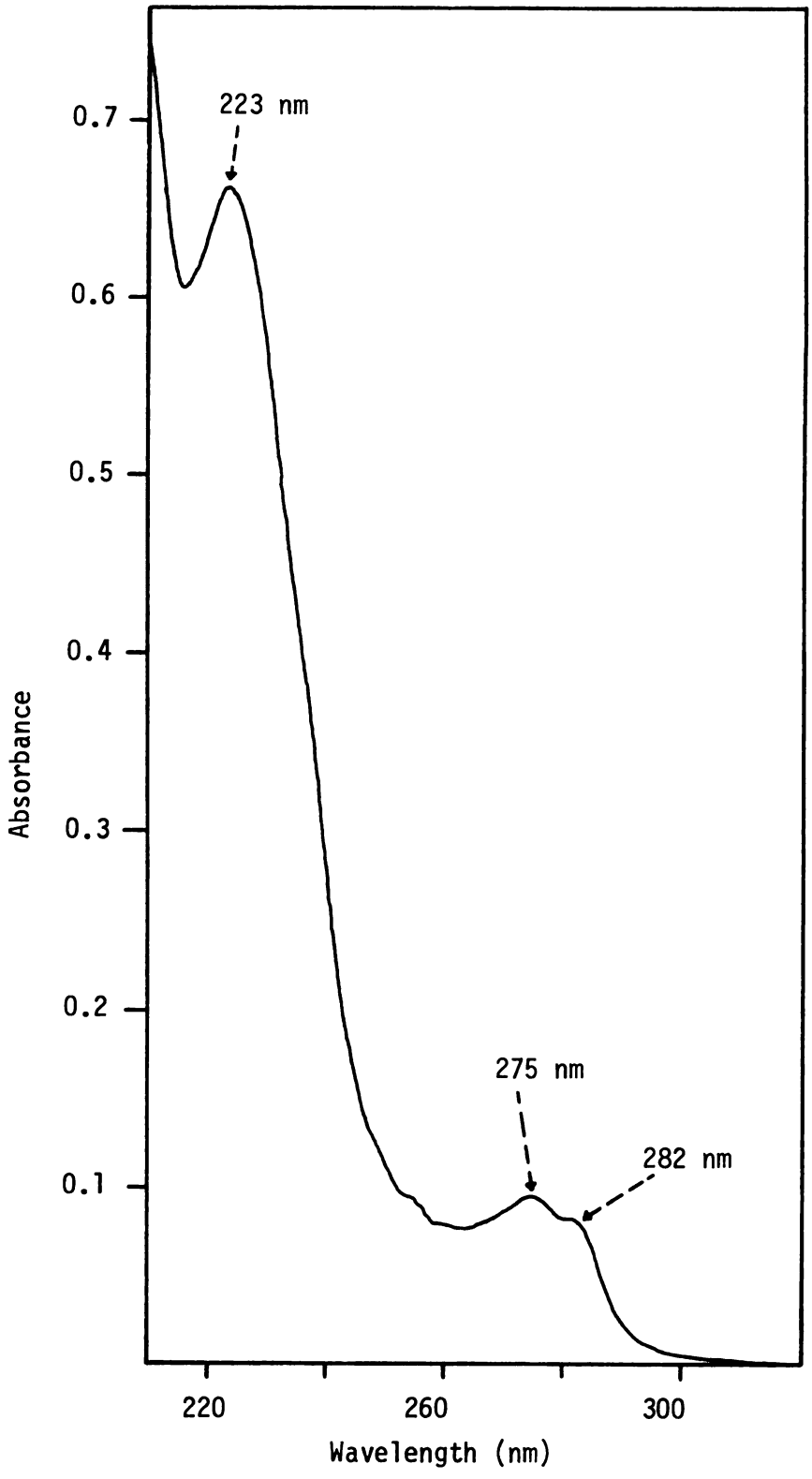

50
100
150
200
250
300
350
X4

Figure 10. Ultra-violet absorption spectrum of di-octylphthalate in hexane (Cary 14 Spectrophotometer).


223 nm
275 nm
282 nm
0.7
0.6
0.5
0.4
0.3
0.2
0.1
Absorbance
220
260
300
Wavelength (nm)

DISCUSSION

These results have shown that the photo-dechlorination of heptachlor is a common reaction following 24 hr exposure at 310 nm as a film on Pyrex glass. Similarly the same photoproducts were found under film conditions when in combination with the long chain alkane, ketone or alcohol as well as when these compounds were photolyzed in solution under the various conditions. It is felt that the monodechlorination which resulted when the alkane or ketone and the carbonyl fraction were photolyzed resulted from photochemical sensitization by di-octyl phtalate which was found to be present in excess of 90%. The absorption of this compound has been shown to be between 290 and 300 nm, as well as at the lower wavelengths could very likely function as a sensitizer in this system, it is necessary to consider that since this class of compounds are prevalent environmental contaminates, this may be a feasible photochemical explanation to a number of questions, such as the accountability for the disappearance of large amounts of pesticides.

According to Flotard (1968) and McGuire (1969), solution photolysis of heptachlor in hexane yielded only the hexachlor isomers at 254 nm in less than 3 hr. Our findings demonstrate that the same photochemical reaction occurs, but at a different wavelength and over a different time period. The formation of these isomers is possible at environmental wavelength's (290-310 nm) and at longer time periods (24 hr to 5 days). At the reported wavelength used and the photolytic time period used in the

various experiments, the yields were not small.

Solution photolysis of heptachlor either in the presence or absence of a sensitizer failed to produce the cage form of heptachlor, as previously reported by Flotard and McGuire. However, the film photolysis of heptachlor in the sunlight, for 3 months resulted in only 15% conversion to the cage form. This is unlike the 90% yield reported by Vollner and Korte (1969) at 254 nm. This is again another case where it is possible to photochemically produce the same photoproduct but the yield is significantly less when using the longer wavelengths.

The photolysis of the heptachlor film on the surface of epicuticular wax can be interpreted in two ways: one being that the formation of the cage form of heptachlor was the result of atmospheric sensitization, since Flotard obtained the cage of heptachlor when photolysis was carried out in acetone, a sensitizing solvent; the other is that the tomato fruit wax applied to the surface of the plate could posses "unknown" sensitizers, which also can facilitate the rearrangement of heptachlor. Baker (1974) defined the epicuticular wax constituents of the tomato fruit as being composed of 77% long chain hydrocarbons, 22% of fatty acids and approximately 1% pentacyclic triterpenoids, in particular, α and β amyrin. The latter class of compounds possesses no sensitizing capacity and therefore the reaction can be only photochemical. The increase of cage formation is the result of the use of the reactor, which speeds product formation due to its greater energy output.

The findings reported by McGuire (1969) that the photolysis of heptachlor in various solvents and acetone resulted in the solvent "adduct" to the C_1 position of the heptachlor molecule, and the subsequent loss of chlorine. This is the only "adduct" type reaction reported to have

occurred, photochemically. This report prompted this investigation as to wheather this reaction was unique only to the set of conditions described by McGuire, or whether this reaction might represent a possible mechanism of inactivating any of the cyclodiene insecticides, thus preventing their further movement through the cuticle. To date there are no reports of any such compounds in the epicuticular layer which might act in this manner. Using the medium chain length compounds verified that in fact this might be a feasible mechanism. Heptachlor was found to dechlorinate and to add the C_{11} alkane at the predicted position; the C_{10} primary alcohol lost the hydroxyl portion of the molecule and also added at the same position. These findings reinforced the supposition that if both short and medium chain compounds could photochemically react at the allyl position of heptachlor, then perhaps this represented one way in which pesticide levels could be reduced (or accounted for) at the plant surface. It warranted further investigation. Using compounds with chain lengths common to the tomato and pear surface waxes the solution and film photolysis of the alkane and the ketone failed to produce the expected photo-addition products obtained in the earlier experiments. Photo-addition of ceryl alcohol was found to occur under the experimental conditions described. This represents the definite possibility for a photochemical interaction at the plant surface. Although the predominance of primary alcohols is low in the epicuticular wax of many plants, their location is ubiquitous in the upper region of the membrane and are more highly associated with the polar regions of the membrane. It is known that ultra-violet light can penetrate through the thin, transparent upper surface so one can assume that a photochemically induced reaction is feasible and that lipophilic insecticides could "dissolve" into and then

photochemically react.

Implications of the Study

A study was undertaken to find any possible photochemical interaction of heptachlor with the primary constituents of tomato and pear surface waxes in order to gain an insight into possible surface interactions. These data suggest the possibility, at least with the alcohol compounds. Equally important is the finding and identification of the hexachlor dimers. This finding alone has a two-fold importance: 1) methodological and 2) environmental.

I. An important aspect common to all past photochemical research with pesticides is that gas chromatographic analysis for the identification of pesticide photoproducts was carried out isothermally, at temperatures between 150° and 200°C, using primarily 6 foot columns. Now, if end photoproducts possess a molecular weight of 550 or greater, as is the case for the hexachlor dimers (mol.wgt.670), it is impossible to find that compound at such low isothermal temperatures. Knowing the maximum operation temperatures for the liquid phase used, the analysis of photoproducts should be carried out over a wide temperature range, starting low and programming at a suitable rate to a temperature perhaps 20° under the recommended maximum temperature for that particular liquid phase. When using combined gas-chromatography-mass spectrometry, the interfacing between the two instruments at times, can forbid the use of such high temperatures employed for gas chromatographic analysis, but may be required to elute the compound(s) from the column. The use of a column one or two feet in length with the same packing, will reduce the necessity for the very high temperatures and the compound can then be identified by this method. II. Another apparent fact when using

combined g.l.c.-m.s. is that many compounds may fail to show a molecular ion at 70eV. This can and does lead to misinterpretation of data, especially when one relies upon tabulated data. One has the option of reducing the ionizing voltage to 25eV (or close to that) which reduces the fragmentation of more labile compounds and increases the probability of finding the parent ion. This reduces the chance of publication of incorrect data.

The environmental implication of these findings, especially with respect to the identification of the dimers poses a considerable number of questions, not only for heptachlor, but for the entire family of cyclodiene insecticides. Experiments appear to leave much to be desired, and should be re-evaluated. But one must now ask if, in fact, these compounds are in the environment. Do they exist in any quantity? What is the toxicity of these compounds? What is their life span, environmentally? Although the parent compounds of most of these chemicals have been banned from further use, what is the possibility that dimerization has occurred to these chemicals. Although we realize that many of these chemicals are applied to the "surface" of the soil or plant, it is essential we remember that all vaporize and in doing so, can feasibly even be sensitized to dimerization. All these questions require consideration. This is especially true in view of the fact that many of the plasticizers absorb in the ultra-violet range important to the environment and could serve as potential sensitizer for such reactions. In 1970, 350 million pounds of plasticizers were released into the environment and since 1948 there has been 8 billion pounds released. The epicuticular components of many plants may still possess the properties of sensitizing the dimerization of insecticides: this requires re-evaluation

or re-investigation. (Silent Spring by Rachel Carlson isn't the only answer, a re-evaluation of analytical techniques seems warranted, also.)

SUMMARY

Monodechlorination of Heptachlor at the vinylic C_5 or the C_6 position has been shown to be a commonly occurring photochemical reaction at 310 nm and under a wide variety of conditions. The percent conversion of these compounds, although variable under varying experimental conditions was high enough to warrant further toxicological research.

Conversion of Heptachlor to its structural isomer, the cage form, occurs in the sunlight in the absence of artificial sensitizers.

Medium chain compounds added at the C_1 position of Heptachlor and the same addition type reaction occurred with the long chain ceryl alcohol, common to cuticular waxes of many plants.

The most significant finding was the discovery of the hexachlor dimer(s). It occurred under a variety of experimental conditions and is an important breakthrough in analytical pesticide research.

FUTURE RESEARCH

This research has opened several new paths for future investigation, both chemically and environmentally.

I. Chemical

a. Toxicity and metabolism of the dimers. Since the analysis of pesticides and their photoproducts has been shown to have several important areas which may have formed and gone undetected; b. the re-evaluation of a number of the cyclodiene pesticides, in lieu of the methodology used in this study.

II. Environmental

a. Investigate the role of plasticizers as potential sensitizers to pesticides for dimerization under natural conditions. For example, the di-octyl phtalates could in combination with a cyclodiene 1) be photolyzed under laboratory conditions using an artificial light source at 300 nm; 2) the plasticizer-pesticide combination could be applied to the plant surface, exposed to direct sunlight over the summer and evaluated.

b. Study "natural" pesticide penetration through the cuticular membrane. The application of a labelled pesticide to the plant at various stages of fruit maturity, followed by removing samples from the fruit at various growth stages, drying the tissue on the inner surface as well as, the cuticular membrane, incinerating and counting radioactivity. This would provide information as to the effect of chemical maturity of the cuticle in the trans-cuticular movement of pesticides.

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APPENDIX

LIST OF CHEMICAL PESTICIDE NAMES

Aldrin - 1,2,3,4,10,10 Hexachloro-1,4,4a,5,8,8a hexahydro -endo-1,4,-exo-5,8-dimethanonaphthalene.

Chlordane - 1,2,4,5,6,7,8,8-Octachloro-2,3,3a,4,7,7a-hexahydro-4,7-methanoindane

Chlordene - 4,5,6,7,8,8-Hexachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene

DDD (TDE) - 2,2,-bis(p-Chlorophenyl)-1, 1 dichloroethane.

DDE-p,p' - 1,1,Dichloro-2,2-bis(p-chlorophenyl)ethylene

DDT-p,p' - 1,1,1-Trichloro-2,2-bis(p-chlorophenyl)ethane

Dieldrin (HEOD) - 1,2,3,4,10,10-Hexachloro-exo-6,7,epoxy-1,4,4a,5,6,7,8,8a-octa-hydro-1,4,-endo-exo-5,8,-dimethanonaphthalene

Endrin - 1,2,3,4,10,10-Hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-endo-endo-5,8-dimethanonaphthalene

Heptachlor - 1,4,5,6,7,8,8-Heptachloro-3a,4,7,7a-tetrahydro-4,7-methano-indene

Heptachlor Epoxide - 1,4,5,6,7,8,8a-Heptachloro-6,7-epoxy-3a,4,7,7a-tetrahydro-4,7-methanoindene

Isodrin - 5,6,7,8,9-Hexachloro-1,2,3,4,4a-5,8,8a-octahydro-1,4-endo-endo-5,8-dimethanonaphthalene

Methoxychlor - 2,2,-bis(p-Methoxyphenyl)-1,1,1-trichloroethane

Mirex - Dodedachloro-octahydro-1,3,4,-methano-2H-cyclobuta cd -pentalene

Nonachlor (cis/trans) - 1,2,3,4,5,6,7,8,8-Nonachloro-3a,4,7,7a-tetrahydro-4,7-methanoindane