Table III. Pesticides Studied for Interference in the Detection and Measurement of Oryzalin

Captan	DCPA
Malathion	Trifluralin
EPN	Chloroxuron
Methoxychlor	Diphenamid
Toxaphene	Nitralin
DDT	Vernolate
Dalapon	CDEC
Diazinon	Alachlor
Azinphosmethyl	Prophos
Carbophenothion	Chloramben
Carbaryl	Chlorbromuron
Disulfoton	Dinoseb
Linuron	CDAA
	Naptalam

of soil and crop tissues. The results have not been corrected for methylation efficiency. Peak height measurements were used in these computations. Figure 1 shows a chromatogram for dimethyloryzalin standard, control soybean seed, and recovery at 0.05 ppm. Methylation check samples using methyl iodide show about 88% efficiency in the conversion of oryzalin to the dimethyl compound. The within day coefficient of variation for the methylation was found to be about 6%. In this laboratory, duplicate recovery samples and methylation check samples are run with each set of experiment samples.

The dimethyl sulfate procedure shows about 90% conversion efficiency for the methylation process with a coefficient of variation of 8%. The average recovery of oryzalin from fortified crops (grapes, broad beans, asparagus, potatoes, wheat) and soil was about 64%. The coefficient of variation for these determinations was 9.3%.

Sensitivity. With the gas chromatograph electrometer set at 1.28×10^{-10} A full scale, the injection of an amount of the dimethyl compound equivalent to 0.438 ng of oryzalin gave an instrument response of 44% FSD. At these conditions, 0.088 ng was readily detected and gave a response of about 10% FSD. Recovery experiments in which 0.25 μg of oryzalin was added to 25 g of soybean seed (0.01 ppm), and a volume of extract equivalent to 0.088 ng was injected into the chromatograph, showed a response of 6% FSD, or about 60% recovery. The control soybean extract showed no peaks and there was no noise in the recorder baseline. Methylation was carried out by the methyl iodide procedure.

Interference Due to Other Pesticides. The pesticides listed in Table III have been studied for interference when using the crop cleanup procedure and methylation with methyl iodide. An amount of pesticide equivalent to the tolerance allowed for soybean seed was added to control soybean seed, both with and without added oryzalin, and assayed according to the procedure. No interference was observed for any of these compounds.

Once carefully optimized, the dimethyl sulfate procedure gave satisfactory derivatization of oryzalin. However, it was found that slight changes in the purity of the reagents and solvent composition led to erratic conversions. Consequently, the method was not considered suitable for residue determinations, although the procedure afforded a rapid conversion. The methyl iodide reaction is considerably slower, but the milder reaction conditions do not lead to decomposition of the oryzalin (which may occur in highly alkaline solutions) and, therefore, this method is clearly preferable for residue determinations of oryzalin.

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Studies of the Degradation of Mirex with an Iron(II) Porphyrin Model System

Roy L. Holmstead

Mirex reacts with reduced hematin to yield products formed from reductive dechlorination which include mono-, di-, tri-, and tetrahydro derivatives as well as other more polar decomposition products. The decomposition is rapid with about half of the Mirex initially present being observed after ca. 13.9 min using an initial molar ratio of Mirex to hematin of 1:5. This iron(II) porphyrin system may serve as a model for understanding Mirex degradation under certain environmental conditions.

The insecticide Mirex (dodecachloropentacyclo[5.3.0.-$0^{2,6}.0^{3,9}.0^{4,8}$]decane, 1) has been used extensively throughout the Southeastern United States to control the imported fire ants *Solenopsis invicta* and *Solenopsis richteri*. A considerable amount of controversy (Alley, 1973) has evolved concerning the use of this chemical, much of which is due to its unusual stability both in laboratory tests and under environmental conditions. Extensive chemical studies on Mirex (McBee et al., 1956; Eaton et al., 1960; Dilling et al., 1967) show this chemical to be thermally stable and resistant to most common oxidizing and reducing systems. Studies on the photochemical stability of Mirex have been carried out both in solution and on solid surfaces. Ultraviolet lamp irradiations of Mirex in aliphatic amines as solvents (Alley et al., 1974) lead to two major photoproducts identified as the monohydro and dihydro derivatives **2** and **4**, whereas, in hydorcarbon solvents (Alley et al., 1973), the major photoproducts were the monohydro and dihydro derivatives **5** and **6**.

The photochemistry of Mirex on silica gel surfaces and chromatoplates using sunlight (Gibson et al., 1972; Ivie et al., 1974a) shows this chemical to decompose slowly with the major photoproduct formed being identified as the

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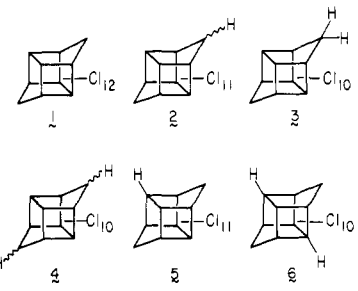


monohydro derivative **5**. A recent study (Ivie et al., 1974b) on the accumulation, distribution, and excretion of [^{14}C]Mirex in rats, quail, and fish showed further that Mirex is highly resistant to in vivo biochemical degradation with a very high potential for accumulation in certain tissues, especially fat, and with these authors concluding that Mirex may be the "most biochemically stable organic pesticide known". Mirex when incubated under anaerobic conditions with sewage sludge yields one breakdown product identified as compound **2** (Andrade and Wheeler, 1974; Ivie et al., 1974a) formed from reductive dechlorination at a *gem*-dichloro group of the parent material. Compounds **2** and/or **5**, also reduced derivatives, were considered likely as possible metabolites of Mirex in the metabolism studies with rats, quail, and fish (Ivie et al., 1974b). Thus, the information to date indicates that reductive dechlorination may be a predominant pathway for Mirex decomposition.

One way to examine possible biological or environmental modes of degradation of chemical pesticides such as Mirex is through the use of appropriate model systems.

The ability of iron(II) porphyrins to reduce alkyl halides has been known for some time (Castro, 1964) and the environmental significance of this general reaction has been noted (Wade and Castro, 1973a). One model system consisting of hematin reduced with sodium dithionite ($Na_2S_2O_4$) has been utilized by several laboratories (Miskus et al., 1965; Zoro et al., 1974) in studying the conversion of the trichloromethyl group of DDT to the dichloromethyl analogue DDD. Moreover, the predicted (Castro, 1971) oxidation of hemoproteins including hemoglobin and myoglobin (Wade and Castro, 1973b; Castro and Bartnicki, 1975) by alkyl halides has been demonstrated. These systems may also serve as appropriate models for the conversion of DDT to DDD by bacteria, yeast, and other microorganisms under anaerobic conditions and by invertebrate animals and blood and liver of birds and mammals following death.

This present study examines the reaction of Mirex with the iron(II) protoporphyrin system, hematin reduced by $Na_2S_2O_4$.

MATERIALS AND METHODS

Chemicals. Technical Mirex (Allied Chemical Corp., Baltimore, Md.) was recrystallized twice from benzene before use. Uniformly labeled [^{14}C]Mirex (5.68 mCi/mmol) was prepared by Mallinckrodt Chemical Works (St. Louis, Mo.). The radiolabeled and unlabeled Mirex samples utilized gave only a single spot on thin-layer chromatography (TLC) in several solvent systems and single symmetrical peaks on gas–liquid chromatography (GC) examination. Analytical standards of reduced products of Mirex including compounds **2**–**6** were obtained from the Mississippi State Chemical Laboratory and shown by TLC and GC to be greater than 95% pure. All other chemicals and solvents used including hematin (ferriprotoporphyrin hydroxide), $Na_2S_2O_4$, triphenyltin chloride, Tween 80, and other chemicals and solvents were of reagent grade quality and used without further purification.

Analysis. *Electron Capture (Ec)–GC.* For routine qualitative and quantitative measurements three GC systems were used: (1) a Varian Aerograph Model 1400 instrument with a ^{63}Ni ec detector and a coiled glass column (3 m × 2 mm i.d.) containing 3% SE-30 on Gas-Chrom Q (80–100 mesh) operated isothermally at a column temperature of 240 °C with a N_2 flow rate of 75 ml/min; (2) a Tracor Model 222 instrument with a ^{63}Ni ec detector and a U-shaped glass column (2 m × 2 mm i.d.) containing 5% DC-200 on Gas-Chrom Q (80–100 mesh) operated at a similar temperature and N_2 flow rate as the Varian instrument; (3) the Varian instrument mentioned above fitted with an open-tubular glass capillary column (15.5 m × 0.25 mm i.d.) containing SE-30 (J. & W. Scientific, Orangevale, Calif.) and operated isothermally at 220 °C using helium at a valve pressure of 10 psi as the carrier gas and N_2 at a valve pressure of 20 psi as a make-up gas. This system was utilized primarily for co-chromatography comparison with authentic standards.

Routine GC–MS and MS. The Finnigan 9500 gas chromatograph coupled to a Finnigan Model 1015D mass spectrometer with a CI source was used in combination with a System Industries Model 150 control system. A U-shaped glass column of 1.2 m × 2 mm i.d. length containing 3% Dexil-300 on Varaport-30 (100–120 mesh) was operated isothermally at 200 °C and a methane flow rate of 20 ml/min (methane pressure of 1–1.5 Torr in the CI source). Solid samples were volatilized upon slowly heating the probe.

Thin-Layer Chromatography (TLC). For TLC, silica gel 60 F-254 chromatoplates (20 × 20 cm, 0.25 mm layer thickness) were developed after spotting in one direction with heptane and in the other with ether–hexane (2:1). ^{14}C-Labeled products were detected by radioautography while unlabeled material was observed by spraying with a 10% solution of diphenylamine in acetone with subsequent uv irradiation.

Reaction of Mirex or [^{14}C]Mirex with Reduced Hematin. A typical reaction procedure was as follows: to a 25-ml Erlenmeyer incubation flask was added a solution of 3.165 mg (5 μmol) of hematin dissolved in 0.5 ml of 0.1 N Na_2CO_3 solution and to this was added 5 ml of distilled H_2O and 1 ml of ethanol containing 25 mg of Tween 80. Excess oxygen was displaced from the flask by blowing a gentle stream of argon over the surface of the resulting mixture and solid $Na_2S_2O_4$ (25 mg) added to the flask with the deaeration being continued. At this point, the solution changes colors from a green to a dark red indicating the presence of the reduced form of hematin. The flask was then covered using a gas-tight rubber stopper with a double seal septum being careful that the contents remained under an argon atmosphere. Through the septum was injected 0.2 ml of ethanol containing 0.546 mg (1 μmol) of Mirex or in the case of the radiolabeled studies, a mixture of 0.519 mg of cold and 0.027 mg of labeled Mirex (total 0.546 mg). The flask(s) were then placed in an incubation shaker at 37 °C for varying reaction times. The concentrations of the reactants initially present in moles/liter were: hematin, 7.5×10^{-4}; Mirex, 1.5×10^{-4}; and $Na_2S_2O_4$, 0.02. Controls showed that all components listed above were necessary in order for the reaction to proceed.

Product Analysis from the Reaction Using Mirex and [^{14}C]Mirex. Work-up of the reaction mixture consists of initially extracting the aqueous solution with 2 × 10 ml of ether. This extraction was followed by acidification of the resulting aqueous fraction to pH 1 using concentrated

HCl and after ca. 20 min extracting the resulting dark brown solution with 2 × 5 ml portions of ether–ethanol (3:1) with 0.5 g of solid $(NH_4)_2SO_4$ added. The ether and ether–ethanol fractions were then analyzed by ec–GC, GC–MS, or, in the case of [^{14}C]Mirex, TLC. Quantitative ec–GC measurements carried out on the initial ether extract were primarily concerned with compounds 1–6 since analytical standards were available.

Elemental compositions of the ether-soluble products in the reaction mixture corresponding to compounds 1–6 were also determined by GC–CI–MS using the appropriate $[M - Cl]^+$ fragment ion.

An alternative qualitative procedure for products of [^{14}C]Mirex reactions involved combination of the ether and ether–ethanol extracts, evaporation of the liquid phase, dissolving the residue in a small amount of ether–ethanol, and TLC separation of the products using radioautography for detection on TLC plates.

Triphenyltin Hydride Reduction Procedure. Reductions of Mirex and control reductions on dehydro derivatives were carried out by treating the caged halocarbons with triphenyltin hydride prepared from the corresponding triphenyltin chloride and $LiAlH_4$ (Kuivila and Beumel, 1961). The hydride (1 or 2 molar equiv) and halocarbon (1 molar equiv) were dissolved in a small amount of heptane and either irradiated at 60 °C with a G.E. sunlamp for 3 h or heated to 100 °C for 2–3 h in a sealed tube in the presence of 2,2'-azobis(2-methylpropionitrile) (AIBN). Analysis by ec–GC or GC–CI–MS was carried out directly on the reaction mixture.

RESULTS

Control reactions using [^{14}C]Mirex demonstrated that in the absence of Tween 80 the mixture was not homogeneous relative to Mirex and greater than 97% of the radiocarbon as Mirex could be found in the initial ether extraction even after 24 h at 37 °C. However, with the addition of a small amount of this detergent, the reaction proceeded smoothly and rapidly. Preliminary studies showed that after 3 h at 37 °C, a reaction mixture composed of a 1:1 molar ratio of hematin to Mirex was somewhat slow in product formation while a 10:1 ratio was too rapid with many of the products observed at early stages in the reaction being totally absent due to further reaction with the excess reduced hematin. However, an intermediate value of 5:1 of hematin to Mirex gave an adequate amount of product formation within a reasonable period of time and, thus, this molar ratio was used throughout the product study. When Mirex is allowed to react with the system described by Wade and Castro (1973a) with hematin as the iron porphyrin and iron powder as the reductant, compounds 2 and 4 are formed. However, in this reaction, product formation with Mirex is extremely slow relative to the above aqueous system and thus it was not utilized in the present study.

As observed by ec–GC analysis, the reaction of Mirex with reduced hematin is rapid yielding numerous products all of which have shorter GC t_R and R_f values on TLC relative to the parent material. Three of these products, observed in largest amounts, show identical chromatography and mass spectrometry characteristics using ec–GC on the packed and glass capillary systems, TLC and GC–CI–MS as authentic samples of compounds 2, 3, and 4. Two other products, formed in considerably smaller amounts and observed late in the reaction sequence by ec–GC, were identified by GC–CI–MS as trihydro and tetrahydro derivatives of Mirex. Several other unknown products, all of very short t_R, were observed in varying amounts upon ec–GC analysis of the reaction mixture. The monohydro and dihydro derivatives 5 and 6 were not observed in any of the product analyses. Initial qualitative examination of reaction mixtures using GC–CI–MS was utilized which demonstrated this to be especially useful in determining the degree of dechlorination of the reaction products. Table I gives the CI–MS data for Mirex and compounds 2 through 6.

Table I. Methane Chemical Ionization Mass Spectra of Mirex and Five Reductive Dechlorinated Derivatives

Compd	(Parent m/e)	m/e (rel. intensities)[a] $[M - Cl]^+$	Other fragment clusters
1	(540)	505 (8.8)	270 (5.8) $[C_5Cl_6]^+$, 235[b] (61.7) $[C_5Cl_5]^+$
2	(506)	471[b] (20.7)	235 (24.5) $[C_5Cl_5]^+$, 201 (16.9) $[C_5HCl_4]^+$
3	(472)	437[b] (24.9)	235 (27.2) $[C_5Cl_5]^+$, 202 (49.9) $[C_5H_2Cl_4]^+$
4	(472)	437 (14.5)	236 (7.4) $[C_5HCl_5]^+$, 201[b] (80.0) $[C_5HCl_4]^+$
5	(506)	471[b] (19.9)	235 (6.0) $[C_5Cl_5]^+$, 201 (18.0) $[C_5HCl_4]^+$
6	(472)	437[b] (25.6)	201 (46.5) $[C_5HCl_4]^+$

[a] Only the first ion of the cluster is reported using the ^{35}Cl isotope. [b] Ion cluster contains the base peak.

In general, the CI–mass spectra of compounds 1–6 were quite simple with very few fragment ions being observed. In all cases the highest fragment corresponds to the $[M - Cl]^+$ ion of the parent molecule and, with compounds 2, 3, 5, and 6, was the cluster containing the base peak. The CI mass spectrum of 1 was similar to that obtained under electron impact (EI) conditions (Dilling and Dilling, 1967) with only the various ion intensities being different especially in respect to the $[M - Cl]^+$ ion which is considerably larger with CI. The methane CI spectra of compounds 2 and 5 gave identical fragments with the intensities varying significantly only with the $[C_5HCl_4]^+$ ion at m/e 202. Unlike compound 1, the cyclopentadiene fragments $[C_5Cl_6]^+$ and $[C_5HCl_5]^+$ (Alley and Layton, 1974) found in the EI spectra of 2 and 5 are not observed in the coresponding methane CI spectra. Compound 3 gives a larger ion at m/e 235 $[C_5Cl_5]^+$ with CI while this is not reported in the corresponding EI spectrum. However, the $[C_5Cl_6]^+$ ion observed for compound 3 with EI is not found with methane CI. Other similarities and differences between the EI and CI fragments are observed with compounds 4 and 6. With these compounds an ion corresponding to $[C_5HCl_4]^+$ is observed both in CI and EI while the $[C_5HCl_5]^+$ ion observed for compound 6 with the EI technique is not found in the corresponding methane CI spectrum. The reasons for these differences are not known but are possibly due to the considerable energy differences between the EI and CI processes.

Figure 1 shows a composite thin-layer radioautogram giving the relative positions of the products formed upon reaction of [^{14}C]Mirex with reduced hematin over a 9-h period. A spot corresponding to [^{14}C]Mirex disappeared totally after ca. 2 h. The monohydro and dihydro derivatives, 2 and 3, cochromatographed in both solvent systems and an intense spot corresponding to these appears soon after combination of reagents and remains varying in intensity, until the 7-h sampling period at which time it is not observed. The dihydro derivative 4 present as a mixture of two isomers, which separate on the TLC system used, is also seen early in the reaction with spots corresponding to this compound being visible even after 24 h. A component chromatographing slightly below 4 is believed to be a mixture of a trihydro and a tetrahydro

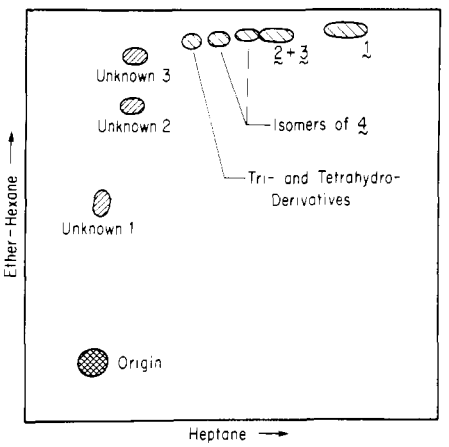


Figure 1. Composite thin-layer radioautogram giving the relative positions of the products formed upon reaction of [^{14}C]Mirex with $Na_2S_2O_4$ reduced hematin.

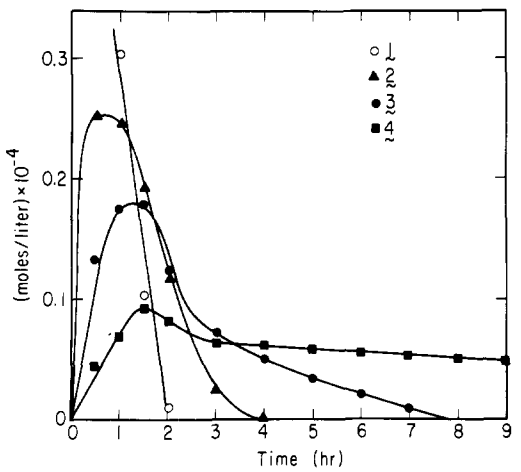
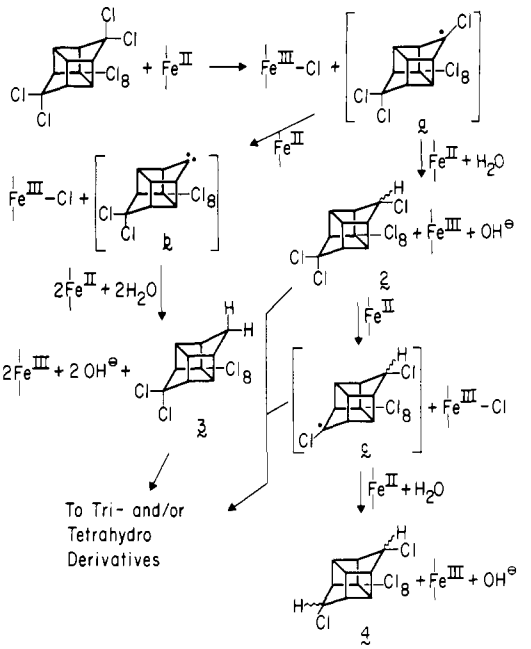


Figure 2. Quantitative results of the reaction of Mirex with $Na_2S_2O_4$ reduced hematin determined from standard concentration curves with authentic samples of **1**, **2**, **3**, and **4**.

derivative of Mirex. Extraction of this spot from several TLC plates with subsequent GC–CI–MS analysis gives two peaks of approximately equal area with fragment ions corresponding to an elemental composition of $C_{10}H_3Cl_9$ at *m/e* (relative intensity) 403 (32) $[M - Cl]^+$, 367 (4) $[C_{10}H_2Cl_7]^+$, 201 (28) $[C_5HCl_4]^+$, and 167 (91) $[C_5H_2Cl_3]^+$ and $C_{10}H_4Cl_8$ at *m/e* (relative intensity) 369 (45) $[M - Cl]^+$, 333 (5) $[C_{10}H_3Cl_6]^+$, 202 (12) $[C_5H_2Cl_4]^+$, and 167 (50) $[C_5H_2Cl_3]^+$ (using ^{35}Cl with only the initial ion of the fragment cluster being reported). Three other unknown components formed in relatively small amounts are also visible at varying times during the reaction. Unknown 1 (R_f 0; 0.46) is formed early in the reaction but is not observed after the 4-h sampling period. Unknown 2 (R_f 0.10; 0.73) appears after about 2 h and remains throughout the reaction period. Unknown 3 (R_f 0.12; 0.88) is observed early and disappears after the 2-h sampling time. A large portion of the radioactivity remained at the origin with the amount observed depending upon the reaction time. Thus, after 9 h, greater than 90% of the radioactivity initially present in the mixture was found at the origin.

The quantitative results of the reaction of Mirex with hematin determined from standard concentration curves with authentic samples of Mirex, **2**, **3**, and **4** are shown in Figure 2. Mirex is observed to decrease in concentration from an initial value of 1.5×10^{-4} to 1.08×10^{-6} M after 2 h under the reaction conditions. The concentration of

Scheme I



compound **2** increases rapidly and reaches a maximum value after about 0.5 h and decreases with time until after ca. 4 h none is observed. The dihydro derivative **3**, although somewhat more slowly than **2**, also reaches a maximum concentration early in the reaction period (ca. 1 h) and decreases at a rate somewhat slower than **2** such that after 8 h none is observed. The other major dihydro component, **4**, slowly reaches a maximum concentration at about 1.5 h after the reaction is started with its concentration decreasing very slowly. Even after a 24-h reaction period, compound **4** is observed at a concentration of ca. 4×10^{-6} M.

Reduction of Mirex using 2 molar equiv of triphenyltin hydride gives products identical with those observed in the hematin reactions. Two other products present in the tin hydride reduction mixtures but not observed in the hematin reductions were components chromatographing with authentic standards of the monohydro derivative **5** and the dihydro compound **6**. However, relative to the total number of products formed in the organotin hydride reductions, compounds **2** and **4** represent the greater proportion of reduced material.

DISCUSSION

Products obtained from in vitro reductive dehalogenation studies with various substrates using iron(II) porphyrin systems have also been observed in vivo (Wade and Castro, 1973a,b). Since studies carried out to date show the major decomposition of Mirex to involve reductive dechlorination (Andrade and Wheeler, 1974; Ivie et al., 1974a), an iron(II) porphyrin system such as reduced hematin is an appropriate model system to study the possible mechanisms for environmental decomposition.

Studies with the reduced hematin model system show that Mirex decomposes very rapidly to give products resulting from reductive dechlorination at the *gem*-dichloro groups as well as unknown products with considerably greater polarity.

A mechanism of the reduction of alkyl halides by iron(II) porphyrins has been delineated (Wade and Castro, 1973a; Castro et al., 1974) and our results indicate that Mirex may follow a similar decomposition pathway involving free-radical, carbene, or carbenoid intermediates. Scheme I gives a mechanistic pathway which may account for the

dechlorinated products observed. Mirex reacts initially with a molecule of reduced hematin to yield the iron(III) protoporphyrin and a free-radical intermediate (**a**). This intermediate may then react further with another molecule of reduced hematin and a proton source to form the monohydro derivative **2**. The rate at which **2** is formed relative to other observed products is quite rapid as seen in Figure 2 with the maximum concentration being reached after ca. 0.5 h. Compound **2** may then react further at the opposite *gem*-dichloro group by a similar radical mechanism to yield intermediate **c** and finally compound **4** in which a mixture of isomers is formed. Compound **3** is initially thought to have originated by a free-radical process occurring on the reduced end of compound **2**. However, the reaction of authentic **2** with reduced hematin yielded only the dihydro derivative **4**, whereas, under alternate free-radical conditions with **2** using triphenyltin hydride, AIBN, and light, both **3** and **4** were formed. Thus, these data indicate that **3** is not being formed from **2** by reacting with reduced hematin through the proposed free-radical pathway. A similarity in reactivity and product formation between iron(II) porphyrin systems and low-valent metal species including Co(II) and Cr(II) toward *gem*-dihalo compounds has been reported (Wade and Castro, 1973a) in which a carbene or carbenoid intermediate is involved (Castro and Kray, 1966). Thus, it is proposed (Scheme I) that intermediate **a**, once formed, may react to form **4** as described above or, by abstraction of another chlorine atom by a molecule of reduced hematin forming a carbene or more likely a complexed carbenoid intermediate. This intermediate species (**b**) may then react by a series of steps (Scheme I) to yield the final product, compound **3**. The trihydro and tetrahydro derivatives observed by GC–CI–MS analysis may arise as shown in Scheme I through either compound **2** or **3** by one of the proposed mechanisms described above. The unknown products observed in the [^{14}C]Mirex studies including those at the origin may possibly result from ring opening of one of the proposed intermediates with subsequent extensive dechlorination or possibly hydroxylation occurring (Castro and Kray, 1966).

Using pseudo-first-order rate constants calculated from the disappearance curves for Mirex and each of the reduction products (Figure 1), approximate half-life values were determined. Under the reaction conditions used, Mirex has a calculated half-life of 13.9 min, monohydro derivative **2** 32.8 min, dihydro derivative **3** 84.4 min, and dihydro derivative **4** 398 min. Thus, stability of the identified reaction products to reduced hematin follows the order Mirex < **2** < **3** < **4**. This order is also observed in reactions carried out for 3 h in which the mole ratio of Mirex to hematin was varied from 1:1 to 1:25. In this case, of the three reduced products only compound **4** was observed in high (1:25) mole ratio reaction mixtures.

Extensive studies with DDT conversion to DDD in anaerobic microsome–NADPH (Walker, 1969) and reduced hematin systems (Miskus et al., 1965; Zoro et al., 1974) and, more recently, similar studies with toxaphene (Khalifa et al., 1976) permit the following prediction for Mirex by analogy: microbial degradation decomposition of Mirex may occur under anaerobic conditions and other reducing conditions such as with sewage sludge; degradation may occur on storage of postmortem blood and other tissue samples and in general on death of animals containing Mirex residues in a manner similar to that shown for DDT to DDD conversion (Zoro et al., 1974). The reduced hematin model system utilized in this present study provides the base point for these speculations and predictions and subsequent investigations on their relevance.

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