Pyrethroid Photodecomposition: Pydrin

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Photolysis of α-cyano-3-phenoxybenzyl α-(4-chlorophenyl)isovalerate (pydrin) in various solvents (hexane, methanol, acetonitrile–water) by artificial light (λ >290 nm) and as a thin film on glass or on cotton by exposure to sunlight yields products resulting from ester cleavage. The major product in solution is formed via photoinduced decarboxylation. The formation of other photoproducts may be rationalized by a mechanism involving free-radical intermediates. 3-Phenoxybenzoyl cyanide and 3-phenoxybenzyl cyanide, two photoproducts observed in solution but not in sunlight, have ip LD_{50}'s to mice of 22 and 105 mg/kg, respectively, and are considerably more toxic than pydrin (LD_{50} > 500 mg/kg).

Pydrin (1) (a Shell trademark, also known as fenvalerate, sumicidin) is a synthetic pyrethroid highly active against a broad spectrum of insects and is more photostable than either the natural pyrethrin esters or earlier synthetic analogues. Pydrin is also unique in that it is the first commercially important pyrethroid lacking the familiar cyclopropane ring functionality associated with other important synthetic analogues such as permethrin and decamethrin (Figure 1). Most of the available data on the photodecomposition (Elliott and Janes, 1973; Ueda et al., 1974; Holmstead et al., 1977; Ruzo et al., 1976; Holmstead et al., 1978) and toxicology of pyrethroids relate to esters containing the cyclopropane ring and are insufficient to predict either the photochemistry of pydrin or the biological activity of its photoproducts.

We report here several photostudies of pydrin using both artificial light sources and sunlight. Some of the work was discussed briefly in our recent review on pyrethroid photochemistry (Holmstead et al., 1977).

MATERIALS AND METHODS

Chemicals. Technical pydrin (Shell Development Co., Modesto, Calif.) was purified by liquid-column chromatography since GLC–MS analysis showed it to contain up to 5% of 3-phenoxybenzaldehyde as well as other minor impurities. All other chemicals utilized in the synthesis were used without additional purification. Solvents utilized in the photolysis were of pesticide grade quality and were deaerated before using. Boiling points and melting points are not corrected.

Preparation and Separation of the Four Pydrin Isomers. *S*(+) and *R*(−) α-isopropyl-4-chlorophenyl acetic acids were prepared and resolved according to the method of Miyakado et al. (1975) via the α-phenylethylamine (Aldrich Chemical Co., Milwaukee, Wis.) salts. Each was esterified by reacting the corresponding acid chlorides with the racemic cyanohydrin prepared in the usual manner. The esters, each consisting of a diastereomeric pair, were separated on a silica gel column by eluting with hexane, or, on a small scale, by using thin-layer chromatography (TLC) with silica gel plates developed three times with hexane–isopropyl ether (4:1). The *SS* and *RR* (first letter refers to the asymmetric carbon bearing the isopropyl group) enantiomeric pair give, as expected, identical GLC retention times (eluting second on the dexil column, Table I) and ^{1}H NMR spectrum: ($CDCl_3$, internal Me_4Si) δ 0.71 (d, 3 H, J = 7 Hz), 0.95 (d, 3 H, J = 7 Hz), 2.30 (bm, 1 H), 3.20 (d, 1 H, J = 10.5 Hz), 6.35 (s, 1 H, CHCN), and 6.85–7.60 ppm (bm, 9 H, aromatic). The *SR* and *RS* pair give the following ^{1}H NMR spectrum: ($CDCl_3$, internal Me_4Si) δ 0.73 (d, 3 H, J = 7 Hz), 1.05 (d, 3 H, J = 7 Hz), 2.30 (bm, 1 H), 3.20 (d, 1 H, J = 10.5 Hz), 6.30 (s, 1 H, CHCN), and 6.85–7.60 ppm (bm, 9 H, aromatic).

Preparation of 3-Phenoxybenzyl Cyanide (9). Utilizing a method described by Zweifel et al. (1970) for the conversion of alcohols to chlorides, 3-phenoxybenzyl chloride was prepared in a 92% overall yield after distillation [bp 123 °C (0.3 mm)] from 3-phenoxybenzyl alcohol (Aldrich Chemical Co., Milwaukee, Wis.). The resulting chloride (10 g, 0.045 mol) was then added to a solution of acetonitrile–DMF (1:1) containing 11.05 g (0.09 mol) of KCN and refluxed overnight. After normal workup and distillation of the resulting dark-brown residue, 8.1 g (89% yield) of pure 3-phenoxybenzyl cyanide [bp 137 °C (0.3 mm)] was obtained giving appropriate IR, mass, and ^{1}H NMR spectra.

Preparation of Decarboxylated Pydrin (2). To ca. 3.9 g (0.1 mol) of freshly prepared sodamide suspended in toluene (Vogel, 1970) is added 18.8 g (0.09 mol) of 3-phenoxybenzyl cyanide. The resulting mixture is warmed to reflux while 18.3 g (0.09 mol) of α-isopropyl-4-chlorobenzyl chloride [prepared by the reaction of isopropyl magnesium bromide (Ventron, Beverly, Mass.) with 4-chlorobenzaldehyde and the resulting alcohol (**16**) being converted to the chloride by the method of Zweifel et al. (1970)] is added dropwise to the solution. The resulting mixture was allowed to stir while refluxing for an additional 4 h. After normal work-up the resulting dark residue was placed on a silica gel column and, with subsequent elution with hexane, yielded 8.3 g (25% overall yield) of pure decarboxylated pydrin described by Holmstead and Fullmer (1977). The decarboxylated pydrin may be further separated into the two diastereomeric pairs by elution with hexane of the racemic material on silica gel.

Preparation of 3-Phenoxybenzoyl Cyanide (4). Using a method similar to that described by Oakwood and Weisberger (1944), 3-phenoxybenzoyl chloride (2.0 g, 8.6 mmol) [prepared from 3-phenoxybenzoic acid and $SOCl_2$] and cuprous cyanide (0.85 g, 9.5 mmol) were heated in an oil bath, first at 150 °C, then at 200 °C for 1.5 h. After cooling, the resulting paste was dissolved in hot benzene, filtered, evaporated to dryness, and recrystallized from hexane–benzene, yielding 1.2 g of pure 3-phenoxybenzoyl cyanide (mp 65–66 °C) with the appropriate IR, mass, and ^{1}H NMR spectra.

Preparation of α-Isopropyl-4-chlorotoluene (13), 2,2-Dimethyl-4-chlorostyrene (14), Dimer (15), and Isopropyl-4-chlorophenyl Ketone (17). To a small one-piece distillation apparatus containing 2.0 g (9.8 mmol) of α-isopropyl-4-chlorobenzyl chloride was added 3.4 g (9.8

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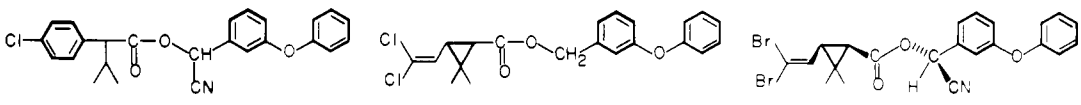

Pydrin (1) Permethrin Decamethrin

Figure 1. Chemical structures of pydrin (racemic mixture of isomers), permethrin (60% trans, 40% cis), decamethrin [(1*R*)-*cis*-α-*S*].

Table I. Photoproducts of Pydrin in Various Solvents as a 0.01 M Solution Using UV Light (λ >290 nm) after 60-Min Irradiation, as a Thin Film on Glass (TF) and on Cotton with Sunlight

Compd[b]	GLC, t_R, min	Percent of total[a] Hexane	Methanol	Acetonitrile–water (60:40)	TF[c]	Present on cotton (+)[d]	Mouse ip LD_{50}[e]
1	16.6, 16.9	8.8	5.4	9.5	61.3	+	>500
2	15.5, 15.8	53.9	68.6	70.4	7.0	+	>500
3	14.3, 14.7	3.8	3.9	1.0	3.7	–	*f*
4	7.2	6.4	4.9	0.0	0.0	–	22
5	7.4	0.0	0.0	1.5	0.5	+	>500
6	5.6	0.0	1.4	0.0	0.0	–	>500
7	6.5	0.0	0.0	0.0	6.2	+	>500
8	5.3	5.6	1.0	0.0	3.4	+	>500
9	7.6	1.2	0.0	0.0	1.3	+	105
10	14.0	1.0	0.0	0.0	0.0	–	*f*
11	13.1	1.0	0.0	0.0	0.0	–	>500
12	4.3	0.0	0.0	6.5	0.5	+	>500
13	1.1	2.4	1.1	0.0	1.7	–	>500
14	1.5	3.5	1.2	0.0	0.8	–	>500
15	10.6, 11.3	7.1	4.2	5.3	0.0	–	>500
16	2.4	0.0	0.0	1.0	2.1	–	>500
17	2.3	0.0	0.0	0.0	4.7	–	>500
Unknowns		5.3	8.3	4.8	6.8	–	*f*

[a] Weigh percent. Values given for compounds having two peaks are the sums of both peaks. [b] See Figure 2 for structures of compounds. [c] Products after 43 days of exposure. [d] Quantitation other than with parent material was not carried out due to limits of detectability. [e] Fifty microliters of methoxy triglycol was used as carrier except for 15 (50 μL of Me_2SO). [f] LD_{50} not determined.

mmol) of triphenyltin hydride (Kuivila et al., 1961). This mixture was heated in an oil bath at 100 °C for 1 h with the hydrocarbon product being distilled under moderate vacuum from the reaction mixture. The styrene analogue was prepared by placing 2.0 g (10.8 mmol) of α-isopropyl-4-chlorobenzyl alcohol (**16**) in a one-piece distillation apparatus with 1 g of 85% H_3PO_4. The mixture was heated at 100 °C for 30 min after which the styrene analogue was distilled under moderate vacuum from the reaction mixture giving 0.85 g of **14**. The dimer (**15**) was prepared by the auto-coupling of the Grignard prepared from α-isopropyl-4-chlorobenzyl chloride (1.93 g, 0.01 mol) with magnesium turnings (0.5 g, 0.02 mol) in ether. The reaction was not worked up in the usual manner but instead, was placed directly on a Florisil column and eluted with hexane. The hexane was removed using a vacuum rotary evaporator with the resulting oil placed on a silica gel column and again eluting with hexane and collecting several fractions. Combinations of the appropriate fractions as determined by GLC gave, after solvent removal, 1.2 g of the desired dimer. The ketone (**17**) was prepared by chromic acid oxidation (Ratcliff and Rodehorst, 1970) of α-isopropyl-4-chlorobenzyl alcohol. All four compounds gave appropriate IR, mass, and ^1H NMR spectra.

Analysis. *Routine GLC–MS and MS.* The Finnigan Model 9500 GLC coupled to a Finnigan 1015D mass spectrometer with a chemical ionization (CI) source was used in combination with a System Industries Model 150 control system for qualitative product analysis. A U-shaped column of 2 m length and 2 mm i.d. containing 3% Dexil-300 on Varaport-30 (100–120 mesh) was operated with temperature programming and a helium flow rate of 15–20 mL/min. Isobutane or methane was used as the reagent gas with a source pressure of 0.5–1.0 Torr. Solid samples were examined using the direct insertion probe.

Chromatography and Analyses. For quantitative analysis data, the Hewlett-Packard Model 5830A instrument equipped with flame ionization (FI) and electron-capture (EC) detectors and a coiled glass column (1.8 m × 2 mm i.d.) containing 3% Dexil-300 on Chromosorb W (AW) 80/100 mesh (Analabs, Inc., New Haven, Conn.) was operated in the programming mode from 130–300 °C at 10 °C/min with a helium flow rate of 15 mL/min. The above GLC was coupled to a Hewlett-Packard Model 18850A GLC terminal. Standard curves were used for quantitation with each of the compounds reported.

For preparative TLC, 20 × 20 chromatoplates coated with silica gel GF (1 mm thick) (Analtech, Inc., Newark, Del.) were eluted with: chloroform–benzene (1:1), hexane–acetone (20:1), hexane–ether (20:1) or (10:1), or benzene (saturated with formic acid)–ether (10:3).

Infrared (IR) spectra were recorded as chloroform or carbon tetrachloride solutions with the Perkin Elmer Model 457 grating IR spectrophotometer. Proton magnetic resonance (^1H NMR) spectra were obtained with the Perkin Elmer R32B 90 MHz spectrometer with spin-decoupling capabilities and using samples dissolved in deuteriochloroform containing 1–3% tetramethylsilane (Me_4Si) as internal standard. Ultraviolet (UV) spectra were obtained on the Perkin Elmer Model 576 double-beam spectrometer.

Photolysis Procedures. Pydrin in solution or in the solid phase was irradiated with UV light (λ >290 nm) or sunlight. The procedures indicated below for pydrin were also applied individually to some of its primary photoproducts.

UV Irradiation. Photolysis studies were carried out by irradiating Pyrex NMR tubes containing 0.01 M solutions of pydrin in methanol, hexane, or acetonitrile–water (60:40). A Rayonet reactor (The Southern N.E. Ultraviolet Co., Middletown, Conn.) and RPR 3000 lamps (peak

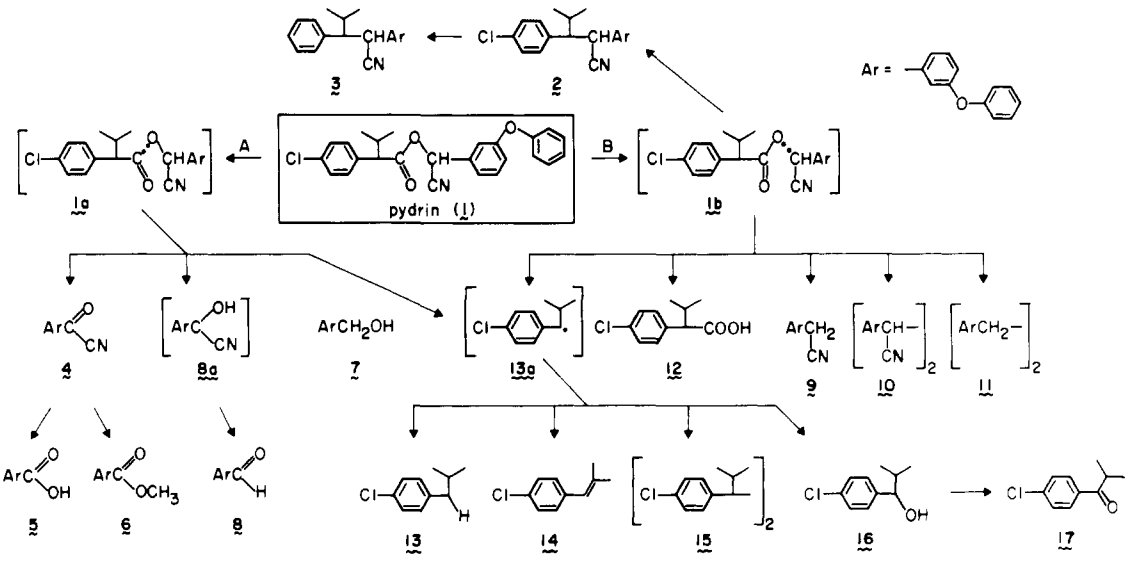

Figure 2. Structures of products listed in Table I and the proposed photochemical pathways to account for the observed products.

output λ 290–320 nm) or RPR 3500 lamps (peak output λ 340–370 nm) were used with the tubes in a "merry-go-round" arrangement within the reactor to insure equal exposure of all samples during the irradiation period. In all cases, "dark" samples were kept as controls. After various irradiation times, a reaction tube was withdrawn for product analysis by GLC or GLC–MS. Large-scale photolyses for product isolation were carried out by dissolving from 1–4 g of pydrin in either methanol or hexane (500–800 mL) and irradiating in a standard Hanovia apparatus using a 200-W medium-pressure lamp with a Pyrex or Corex filter. Separation and isolation of the products was accomplished using a combination of column and thin-layer chromatographic techniques described above.

For studies on glass surfaces, pydrin (10 mg) in ethyl acetate (1 mL) was evaporated on a 10-cm petri dish leaving a thin film (TF) of material. The petri dishes were covered (Pyrex cover) and placed in direct sunlight during the months of July and August in Concord, Calif. where the average ambient temperature varied from 19–43 °C. After various exposure times, the residue was transferred to a vial in ethyl acetate for subsequent GLC and GLC–MS analysis.

Pydrin (emulsifiable concentrate ca. 2.4 lb/gal) was sprayed using an air-pressurized handsprayer with three nozzles on 4–5-week-old cotton plants (ca. 30 cm high) located at Davis, Calif. in mid-July. Three replicate samples each containing three plants were weighed and then placed in a jar and extracted 3 × 100 mL with ethyl acetate. The residue, after removing solvent from the extract on a vacuum rotary evaporator, was transferred with small volumes of ethyl acetate to glass columns (2 cm i.d.) containing 20 g of Florisil dry packed topped with 2 cm of anhydrous sodium sulfate. After residue transfer, 2 cm additional sodium sulfate was added to the column. Enough hexane was added to wet all the packing followed by 150 mL of hexane–ethyl acetate (19:1). The eluent collected was made up to 150 mL for subsequent GLC–EC analysis. Control experiments showed the extraction and clean-up procedure to be 90% efficient.

Acute Toxicity to Mice. LD_{50} values were determined for male albino Swiss Webster mice (18 to 20 g) 24 h after ip administration of the photoproduct. Methoxytriglycol (50 μL) was used as the carrier vehicle except with compound **15** where, because of low solubility, dimethyl sulfoxide (50 μL) was used. Compounds were either shown to be "nontoxic" (LD_{50} >500 mg/kg) in the initial tests or, if not, subsequent tests (using ca. 30 mice/compound) were done to establish a more exact LD_{50}. In toxicant plus synergist tests, the synergist [PB (150 mg/kg); DEF (50 mg/kg)] was injected 1 h (PB) or 6 h (DEF) before the toxicant.

RESULTS

Solution Photodecompositon. The solution phase photodecomposition of pydrin as 0.01 M methanol, hexane, or acetonitrile–water (60:40) solutions is rapid with the half-life values calculated from the initial rate constant (k, 0–30% reaction) being 18, 18, and 16 min, respectively.

Table I gives the quantities of products observed after 60-min irradiation of the various solutions with the corresponding structures shown in Figure 2. Analysis of samples at times prior to 60 min showed those products in Table I to be present, varying only in the relative amounts. Pydrin (**1**), decarboxylated pydrin (**2**), compound **3**, and dimer (**15**) were observed in all three solvent systems. After 60 min of exposure in any of the solvents, less than 10% of starting pydrin remained. No other products containing the original ester linkage were observed, and the major product was decarboxylated pydrin (**2**). Compound **2** accounts for ca. 54% of the total reaction mixture in hexane and ca. 70% in the acetonitrile–water system. Compound **2** and **3** give, as does pydrin, two peaks under the GLC conditions used due to the two diastereomeric pairs (i.e., *RR*, *SS*, *RS*, *SR*). The two peaks observed for the dimer (**15**) are presumably due to the *d,l* and meso forms. The values given in Table I for compounds **1–3** and **15** are the sum of the individual percent yields. Compounds **4**, **8**, **13**, and **14** were observed only with hexane or methanol as solvent. The benzoyl cyanide (**4**) is found in approximately equal but minor amounts (ca. 5–6.5%) in these two solvents. Compounds **8**, **13**, and **14**, also minor products, form in slightly larger amounts in hexane than in methanol. 3-Phenoxybenzylcyanide (**9**) and the dimers (**10**) and (**11**) are found only in the hexane irradiations and are very minor products (ca. 1%). Compound **6**, the methyl ester of 3-phenoxybenzoic acid, is also found in small amounts and only in the methanol solvent. Products unique to acetonitrile–water are the acid **12** and trace amounts of **5** and **16**. Products shown in Figure 2 which are not observed in the solution studies are **7** and **17**. Several unknowns were observed with their yields ranging from ca. 5–10% of the total. The number

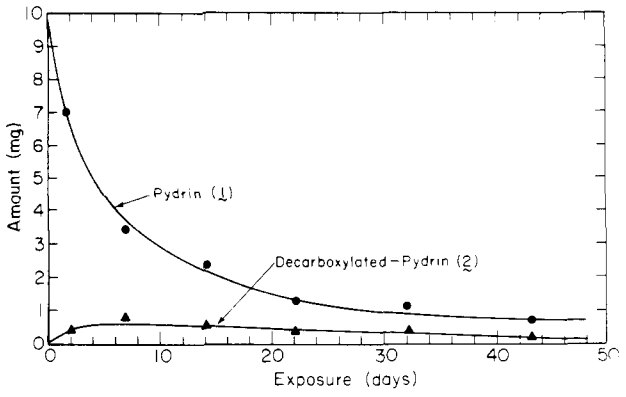

Figure 3. Rate of disappearance of pydrin (1, ●) as a thin film on glass with sunlight exposure and formation of the primary photoproduct, decarboxylated pydrin (2, ▲).

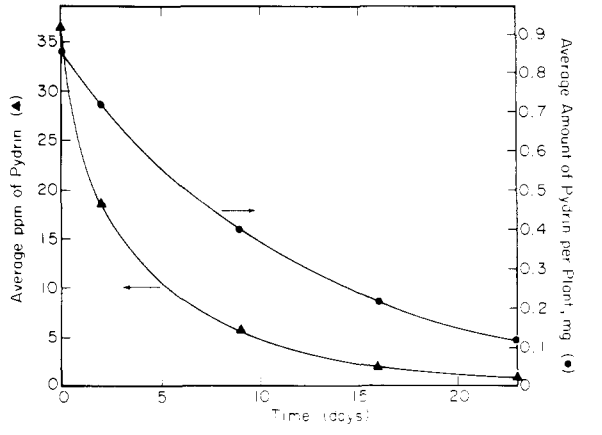

Figure 4. Rate of disappearance of pydrin on cotton in sunlight exposure expressed as: (1) average amount of parent pydrin per plant (mg) (●), (2) average parts per million of pydrin (▲).

of unknowns varied from 2–6 depending on solvent, and all but one had GLC t_R shorter than starting pydrin. In order to investigate the nature of the excited state(s) involved in pydrin photoreactions, sensitization using isobutyrophenone (0.1 M) and quenching with 1,3-cyclohexadiene (0.1 M) in hexane was attempted. No energy transfer from isobutyrophenone was observed; however, the diene quenched the reaction efficiently.

Thin Film (TF) on Glass Photodecomposition. Figure 3 shows the overall decomposition rate of pydrin as a TF on glass in sunlight. The time for half of the initial deposits to decompose under the conditions used was ca. 4 days. About 10% of the pydrin initially applied to the plate remained after 43 days of exposure, the sampling time used for product quantitation where the product/pydrin ratio was the greatest. Figure 3 also shows the amount of decarboxylated pydrin (**2**), the product observed in largest amount throughout the sampling period. Analysis of the residue obtained from the TF experiments showed parent pydrin to be the major component (Table I). Many of the photoproducts in the solution irradiations are also found in sunlight TF, including **2**, **3**, **5**, **8**, **9**, and **12–16**. Compounds **7** and **17**, two products not observed in solution, are also present. As with the solution studies, several unknowns (6) were observed with two being more polar than pydrin on the dexil column.

Photodecomposition on Cotton. Figure 4 shows the overall decomposition rate of pydrin (1) on cotton. The initial deposit of pydrin was about 0.8 mg/plant with half the material remaining after 8 days of exposure. The last sample (23 days) showed about 0.1 mg/plant remaining. The lower curve (Figure 4) takes into consideration the

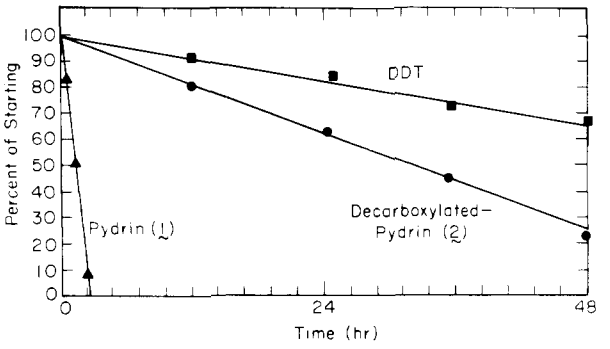

Figure 5. Difference in decomposition rate of pydrin (1), the primary photoproduct, decarboxylated pydrin (2), and p,p'-DDT as 0.001 M acetonitrile solutions in UV light.

growth rate of the plant with the average parts per million of pydrin being given. The initial pydrin concentration was about 35 ppm which dropped to half that amount in approximately 2 days. At the 23-day sampling period, very low levels (<1 ppm) remained. Other compounds which were observed on the cotton plants but not quantitated were **2**, **5**, **7–9**, and **12**.

Stability of Photoproducts. Figure 5 shows the relative rates of photodecomposition of pydrin (**1**) and decarboxylated pydrin (**2**) compared to *p,p'*-DDT as 0.001 M acetonitrile solutions. Although **2** decomposes at a rate somewhat faster than *p,p'*-DDT, it is considerably more stable than the parent ester. When compound **2** was irradiated for 40 h as a 0.07 M methanol solution at 260 and 300 nm, the rate of decomposition was sevenfold faster at the lower wavelength (14% reacted), but the products were identical. The major products arose from reductive dechlorination of **2** to yield **3** (Figure 2) (32% of total product formation). Other photoproducts detected resulted from either photonucleophilic substitution of Cl by methoxy at the para position of the ring or products resulting from cleavage of the diphenyl ether linkage. These structural assignments, based on mass spectral patterns were supported by analogous data from a reaction carried out in CD_3OD. When compound **2** was irradiated as a TF on glass using sunlight no decomposition was detected after 40 days of exposure. With the exception of compounds **2** and **3**, the dimers **10**, **11**, and **15** and compounds **13** and **14**, the other photoproducts (Figure 2), showed no unusual photostability. Photolysis of solutions of the benzoyl cyanide (**4**) showed this material to be relatively unstable, yielding the corresponding carboxylic acid (**5**) in the presence of water or the methyl ester in methanol. The benzyl cyanide (**9**) irradiated in aqueous solutions or on solid surfaces in the atmosphere gave primarily the corresponding alcohol (**7**). The cyanohydrin (**8a**) forms the aldehyde (**8**) upon photolysis more rapidly than in the dark.

Toxicity of Photoproducts. The LD_{50} values for pydrin and its photoproducts were determined by ip injection to mice (Table I) and show that only two of the photoproducts exhibit toxicities greater than the parent material, namely, the benzoyl cyanide (**4**) and the benzyl cyanide (**9**) (LD_{50} values of 22 and 105 mg/kg, respectively). Although the parent material exhibits a greater toxicity if the mouse is pretreated with piperonyl butoxide (PB) or *S,S,S*-tributyl phosphorotrithioate (DEF) (i.e., from >500 to 0.2 mg/kg with PB and to 0.4 mg/kg with DEF), the photoproducts are not significantly synergized by these materials. Compounds **3** and **10** were not individually tested due to the insufficient quantities available. The residue obtained from the sunlight TF experiments

showed a toxicity of >500 mg/kg.

DISCUSSION

The UV spectrum of 1 in ethanol exhibits the allowed $\pi-\pi^*$ transition of the phenyl rings at 204 nm (ϵ 33 700) and a band at 276 nm (ϵ 3400), which is presumably $n-\pi^*$ in character, resulting from the combined transitions of the carbonyl system and the lower energy band of the aromatic rings. These $n-\pi^*$ and $\pi-\pi^*$ transitions can result in the formation of either singlet or triplet excited states and, thus, no unique excited state need be invoked to explain the variety of photoreactions observed by the various functional groups of 1.

The rate of decomposition of cyclopropane ring-containing pyrethroids in various organic solvents has been shown to depend on the polarity of the solvent (Ruzo et al., 1977; Holmstead et al., 1978). This, however, does not seem to be the case with pydrin where solvent polarity has little or no effect, indicating an excited state or activated complex adequately stabilized within the molecule itself and not influenced significantly by its electronic environment.

Figure 2 gives the photolysis sequence for pydrin under various irradiation conditions. The rate of disappearance and product distribution depends upon the reaction phase and upon the irradiation wavelength and intensity. All the photoproducts identified from UV irradiation in solution and in the solid phase involve cleavage of an ester bond. The products obtained can be rationalized as originating from either process A or B (Figure 2).

Photochemical cleavage via pathway A (Figure 2) involves bond breaking between the carbonyl carbon and the oxygen atom (**1a**). The radical associated with the alcohol portion of the molecule may then either lose a hydrogen atom to form the benzoyl cyanide (**4**) or abstract a hydrogen atom to give intermediate (**8a**) which under the reaction conditions eliminates HCN, yielding the aldehyde (**8**). Compound **4**, although observed in the methanol studies, is relatively unstable in protic solvents and reacts further to form the methyl ester (**6**). Compound **4** is less stable to nucleophilic attack in aqueous solutions and hydrolyzes completely to the acid (**5**) in the acetonitrile–water solvent system. The overall reactivity of the benzoyl cyanide toward hydrolysis is less than that of the corresponding acid chloride. This added stability is presumably due to the extensive π system available with the nitrile group as compared to the halogen. Examination of the products resulting from the acid portion of the molecule (**13–17**) indicates that the acyl radical (pathway A) formed must eliminate CO to form the stable benzyl radical (**13a**). This radical then may abstract a proton (**13**), eliminate a proton (**14**), dimerize (**15**), or react with water (**16**). We were somewhat surprised at the relatively large amount of dimer **15** found in the three solvent systems employed which seems to indicate either close proximity of the excited state of the pydrin molecule or long-lived radical intermediates. Compound **16**, as expected, is only observed in systems where water is present, and the ketone (**17**) was observed only in the TF experiments where oxidation is possible.

Pathway B (Figure 2) which involves cleavage of the benzyl carbon–oxygen bond yielding (**1b**) is evidently the preferred pathway in the solution as well as the solid-phase photodecomposition reactions based on the yields of products observed. The major photoproduct, decarboxylated pydrin (**2**), forms by loss of CO_2 from intermediate (**1b**) (Holmstead and Fullmer, 1977). The extensive formation of **2** suggests that a concerted process involving simultaneous combination and loss of CO_2 might be involved rather than simple coupling of the discrete free radicals after loss of CO_2 from intermediate **1b**. However, when single pydrin isomers (i.e., *SR* and *SS*) were irradiated individually in methanol or acetonitrile using conditions identical with those for the racemic **1**, each pure isomer yielded the same racemic mixture of **2**. Discrete separate free radical intermediates are therefore involved in the decarboxylation process under the conditions used. Compound **2** may further react to **3**, but this is a minor process because **2** is relatively stable. Intermediate **13a** instead of coupling with the α-cyano-3-phenoxybenzyl radical may react in a manner similar to that described in pathway A to form **13–16**. Compounds **9** and **12** result from direct abstraction of a proton from a neighboring solvent molecule or other source by each radical portion of intermediate **1b**. Although compounds **9** and **12** are observed in relatively minor amounts (Table I) in the systems previously described, at longer wavelengths (λ >350 nm) and in solution, **9** and **12** were formed in considerably larger amounts. Formation of 3-phenoxybenzyl alcohol (**7**) in sunlight but not UV would tend to support the longer wavelength results since **7** probably originates from hydrolysis of the benzyl cyanide (**9**) after formation. The dimers **10** and **11** may also arise either directly (compound **10**) or indirectly (compound **11**) from intermediate (**1b**), but an exact mechanism to account for the formation of **11** is still in question.

Sensitization and quenching results parallel those reported for other esters (Matuszewski et al., 1973). Triplet sensitizers such as isobutyrophenone are ineffective, and although quenching is efficient, this may be due to interaction of the quencher with a long-lived singlet state. We are continuing attempts to assign excited intermediates for pydrin and other pyrethroids.

In the presence of sunlight and in the solid state as a TF or on cotton, pydrin, as would be expected, decomposes at a much slower rate than was found in the laboratory studies. Under similar conditions on cotton with sunlight, pydrin disappears at a rate intermediate between decamethrin (least stable) (Figure 1) (Ruzo et al., 1977) and permethrin (Figure 1) (Gaughan and Casida, 1978). The levels of the photoproducts on cotton were too low to be determined quantitatively by the methods available.

Most of the photoproducts of **1** are as toxic or less toxic on an acute basis to mice than **1** itself. Compounds **4** and **9**, however, were considerably more toxic than **1** and symptoms in mice treated resemble those of cyanide poisoning (Ohkawa et al., 1972). Perhaps significant in this regard is the observation that neither compound was observed in the cotton studies while only small amounts of **9** were found as a TF on glass. Compounds **5** and **7**, observed in the cotton experiments, may result from **4** and **9**. Mutagenesis tests carried out on compounds **1**, **2**, and **4** using the TA-100 strain of *Salmonella typhimurium* fortified with liver (S-9) homogenate were negative in the formation of mutagen induced revertants.

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LITERATURE CITED

Elliott, M., Janes, N. F., in "Pyrethrum the Natural Insecticide", Casida, J. E., Ed., Academic Press, New York, N. Y., 1973, p 84.

Gaughan, L., Casida, J. E., *J. Agric. Food Chem.* **26**, 525 (1978).

Holmstead, R. L., Casida, J. E., Ruzo, L. O., *Adv. Chem. Ser.* **No. 42**, 137 (1977).
Holmstead, R. L., Casida, J. E., Ruzo, L. O., Fullmer, D. G., *J. Agric. Food Chem.* **26**, 590 (1978).
Homstead, R. L., Fullmer, D. G., *J. Agric. Food Chem.* **25**, 56 (1977).
Kuivila, H. G., Beumel, O. F., *J. Am. Chem. Soc.* **83**, 1246 (1961).
Matuszewski, B, Givens, R. S., Neywick, C., *J. Am. Chem. Soc.* **95**, 595 (1973).
Miyakado, M., Ohno, N., Okuno, Y., Hirano, M., Fujimoto, K., Yoshioka, H., *Agric. Biol. Chem.* **39**, 267 (1975).
Oakwood, T. S., Weisgerber, C. A., *Org. Synth.* **24**, 14 (1944).
Ohkawa, H. Ohkawa, R. Yamamoto, I., Casida, J. E., *Pestic. Biochem. Physiol.* **2**, 95 (1972).
Ratcliffe, R., Rodehorst, R., *J. Org. Chem.* **35**, 4000 (1970).
Ruzo, L. O., Holmstead, R. L., Casida, J. E., *Tetrahedron. Lett.*, 3045 (1976).
Ruzo, L. O., Holmstead, R. L., Casida, J. E., *J. Agric. Food Chem.* **25**, 1385 (1977).
Ueda, K., Gaughan, L. C., Casida, J. E., *J. Agric. Food Chem.* **22**, 212 (1974).
Vogel, A. I., in "A Textbook of Practical Organic Chemistry", Longman Group Limited, London, England , 1970, p 902.
Zweifel, G., Horng, A., Snow, J. T., *J. Am. Chem. Soc.* **92**, 1427 (1970).

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Conversion and Disappearance of Methidathion on Thin Layers of Dry Soil

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A technique has been developed for the production of reproducible thin layers of pesticide-containing soil for studies involving residue behavior on air-dry soil under different environmental conditions. The method has been applied to the study of methidathion on six different soils under conditions simulating those occurring on arid land soil surfaces and under abnormally high ozone levels in air. In contrast to results found for methidathion in moist soils, a very slow rate of disappearance occurs in dry soils in the absence of atmospheric oxidants or sunlight. The initial disappearance of methidathion appears to follow first-order kinetics, but with wide rate variations ($t_{1/2}$ = 19 to 110 days for the particular types of soils tested). Considerable quantities of methidathion oxygen analogue are produced and retained in dry soil, in contrast to very low amounts found by others for moist soil.

The use of pesticides leads to unavoidable contamination of the surrounding soil. Thus, information on pesticide interaction with the soil and its associated soil microorganisms is necessary even for pesticides which were never intended for use as soil treatment chemicals. As water provides a medium for chemical reactions such as hydrolysis and is required for the active existence of soil microorganisms, soil studies generally are conducted under moist soil conditions. Flooded soil conditions, such as encountered in rice paddies, are recognized to yield quite dissimilar results compared to nonflooded conditions (Sethunathan, 1972). The other extreme, represented by air-dry soil, is also a fruitful area of research, as in many areas of the country much of the soil surface remains dry throughout the year. The conversion of organophosphorus compounds containing the P=S moiety to their more toxic cholinesterase-inhibiting P=O oxygen analogues, often called "oxons", on dust adhering to crop foliage (Gunther et al., 1977) demonstrates the importance of this line of investigations. Air-dry soil exposed to sunlight may produce and retain alteration products, such as the oxons, which are not found in any significant quantities in moist soil laboratory conditions. Exposure of agricultural workers to residues of organophosphorus oxons on foliage is speculated to be responsible for the occasional episodes of worker illnesses reported in California (Spear et al., 1975).

Adams et al. (1976) studied the behavior of different parathion-bearing soil dusts resident on citrus leaves. They found that the rate of dissipation of parathion and its extent of conversion to paraoxon were dependent on the characteristics of the soil dust used. Spencer et al. (1975) reported on a sampling technique for soil dust in the field and on the levels of parathion and paraoxon found on the loose surface dust after parathion application to citrus trees.

Here we have used a modification of the soil thin-layer chromatography method of Helling and Turner (1968), who used finely sieved soil in place of conventional adsorbents to produce soil thin-layer plates. By "spotting" a pesticide on the plate and developing it with water, Helling (1971a,b,c) conveniently studied pesticide mobility in soil. In our work, the pesticide was mixed with soil and water and the slurry was spread to produce a 1-mm thickness of soil on glass plates; the soil was allowed to dry and was analyzed at various times for the pesticide and its conversion product. This technique provides a more convenient and reproducible tool for the evaluation of environmental effects such as solar radiation, humidity, and atmospheric oxidants on air-dry soil than is possible with field application studies. The soil thin-layers give an indication of what may occur to pesticides sorbed to dust particles adhering to foliage and on the surface soil of agricultural land. Reported here are tests conducted with methidathion (Supracide, GS-13005, *S*-[5-methoxy-2-oxo-1,3,4-thiadiazol-3(2*H*)-yl)-methyl] *O,O*-dimethyl phosphorodithioate) to determine what effects different soil types and ozone have on its dissipation and its conversion to methidathion oxon under air-dry conditions. This compound was selected as it is currently the third most-used organophosphorus pesticide in California citrus production. Its use here is primarily as a research tool for

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