

- Turner, W. V., Khalifa, S., Casida, J. E., *J. Agric. Food Chem.* **23**, 991 (1975).  
 Turner, W. V., Engel, J. L., Casida, J. E., *J. Agric. Food Chem.* **25**, 1394 (1977).  
 Wade, R. S., Castro, C. E., *J. Am. Chem. Soc.* **95**, 226 (1973).  
 Williamson, K. L., *J. Am. Chem. Soc.* **85**, 516 (1963).  
 Wong, R. Y., Palmer, K. J., Saleh, M. A., Casida, J. E., in preparation (1978).

- Zweig, G., Sherma, J., *Anal. Methods Pestic., Plant Growth Regul.* **6**, 514 (1972).

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## Pyrethroid Photodecomposition: Permethrin

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Photolysis of 3-phenoxybenzyl (1*RS*)-*trans*- or (1*RS*)-*cis*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate (permethrin) in various solvents (hexane, methanol, water, and water-acetone) with artificial light ( $\lambda > 290$  nm) and on soil in sunlight results primarily in cyclopropane ring isomerization and ester cleavage to 3-phenoxybenzyl alcohol and the dichlorovinyl acids. Other photoproducts, often in trace amounts, from *trans*- and *cis*-permethrin are: monochloropermethrin formed by reductive dechlorination and its monochlorovinyl acid cleavage product; 3-phenoxybenzyl 3,3-dimethylacrylate; 3-phenoxybenzaldehyde and the corresponding acid; benzyl and 3-hydroxybenzyl alcohols and the corresponding aldehydes and acids. Permethrin and monochloropermethrin do not undergo epoxidation at the dichlorovinyl or chlorovinyl substituent under normal photooxidative conditions.

Permethrin (also known as NRDC 143) (Elliott et al., 1973) combines high insecticidal activity and low mammalian toxicity with enhanced photostability as compared with earlier synthetic pyrethroids (Elliott, 1977). The available knowledge on pyrethroid photochemistry is based primarily on chrysanthemates (Elliott and Janes, 1973; Ueda et al., 1974) rather than on compounds, such as permethrin, where the photolabile isobutenyl group is replaced with the more photostable dichlorovinyl substituent. We examined the photodecomposition of (1*RS*)-*trans*- and (1*RS*)-*cis*-permethrin in various solvents and on soil utilizing artificial and natural light sources. Some of the results were discussed in our recent review on pyrethroid photochemistry (Holmstead et al., 1977).

### MATERIALS AND METHODS

**Chemicals.** The compounds are designated as shown in Figure 1, which also gives the  $^{14}\text{C}$  positions in acid-labeled (1*RS*)-*trans*- and (1*RS*)-*cis*-permethrin (*t*- and *c*-per, respectively) ( $\text{Ac}^* -58.2$  mCi/mmol) and alcohol-labeled *t*- and *c*-per ( $\text{Alc}^* -55.9$  mCi/mmol). The individual  $^{14}\text{C}$  *t*- and *c*-per isomers (>99% radiochemical purity) were separated from labeled (1*RS*)-*trans*,*cis*-per by thin-layer chromatography (TLC) using solvent system CBX2 described below.

FMC Corp. (Middleport, N.Y.) provided unlabeled *t*- and *c*-per (>99% purity), the corresponding dichlorovinyl acids (*t*- and *c*- $\text{Cl}_2\text{CA}$ ; >99% purity) and (1*RS*)-*trans*-monochloro-per (*E*:*Z* = 1:1): proton magnetic resonance ( $^1\text{H}$  NMR) ( $\text{CDCl}_3$ , internal  $\text{Me}_4\text{Si}$ )  $\delta$  1.15 (s, 3 H), 1.22 (s, 1.5 H), 1.28 (s, 1.5 H), 1.63 (d, 1 H,  $J = 5.5$  Hz), 2.07 (dd, 0.5 H,  $J = 5.5, 8$  Hz, cyclopropyl, *E*), 2.45 (dd, 0.5 H,  $J = 5.5, 8$  Hz, cyclopropyl, *Z*), 5.09 (s, 2 H, benzyl), 5.48 (apparent triplet, 0.5 H,  $J = \text{ca. } 8$  Hz, vinyl, *Z*), 5.65 (dd, 0.5 H,  $J = 8, 13.5$  Hz, vinyl, *E*), 6.08 (d, 0.5 H,  $J = 13.5$  Hz, vinyl *E*), 6.13 (brd, 0.5 H,  $J = 7$  Hz, vinyl, *Z*), and 6.85–7.5 ppm (bm, 9 H, aromatic).

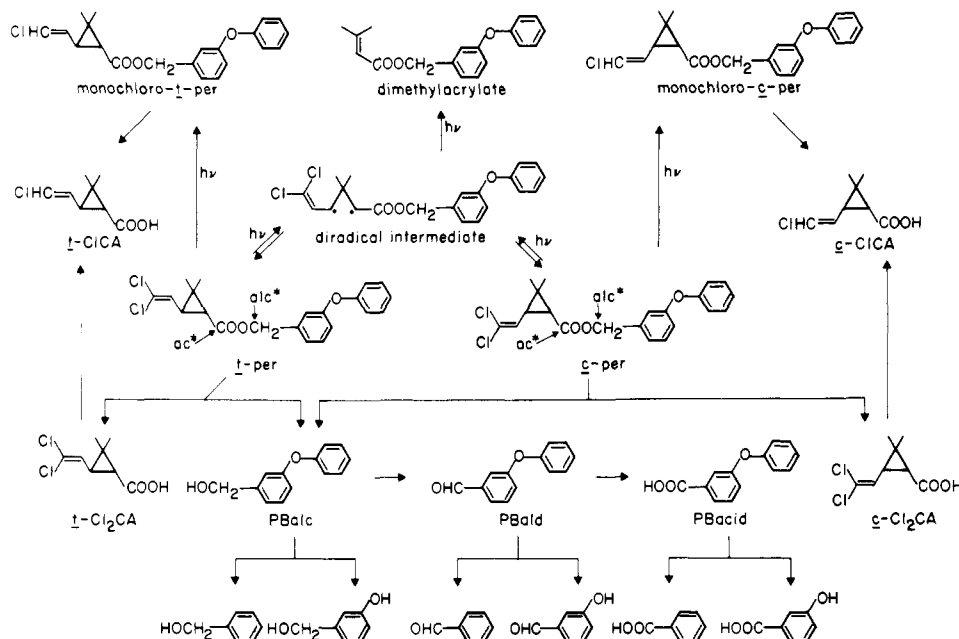
Other standards for comparison with per photoproducts were obtained from Aldrich Chemical Co. (Milwaukee, Wis.) and used without further purification. [ $\text{C}=\text{O}$ ]2,4-Dichlorophenoxyacetic acid (2,4-D) (10.2 mCi/mmol) from New England Nuclear Corp. (Boston, Mass.) was purified by TLC in solvent system CFEX2 (see below). Solvents of pesticide grade quality were deaerated before use in photodecomposition studies.

**Chromatography and Analysis.** Photolysis products of unlabeled *t*- and *c*-per were analyzed by gas-liquid chromatography (GLC) utilizing a Varian Aerograph Model 1400 instrument with a flame ionization detector and a glass column (1.8 m  $\times$  2 mm i.d.) with either 3% OV-101 on Chromosorb W (60–80 mesh) A/W (DCMS treated) or 3% Dexil 300 on Varaport-30 (100–120 mesh). The column temperature was maintained at 250 °C with a  $\text{N}_2$  flow rate of 75 mL/min.

Chromatoplates (20  $\times$  20 cm) precoated with silica gel F-254 (fluorescent indicator) (0.25 mm) (EM Laboratories, Inc., Elmsford, N.Y.) or with silica gel GF (1 mm) (Analtech, Inc., Newark, Del.) were used for analytical and preparative TLC, respectively in the following solvent systems: carbon tetrachloride-benzene (4:1) (CB); benzene (saturated with formic acid)-ether (10:3) (BFE); chloroform (saturated with formic acid)-ether (10:3) (CFE). The resolved products were detected by their quenching of gel fluorescence under short wavelength UV light. Radioactive gel regions detected by radioautography were scraped free from the glass support for liquid scintillation counting (LSC) or for product recovery by extraction of the gel with ethyl acetate, methanol, or other solvents as required followed by cochromatography with unlabeled standards.

**Spectroscopy.**  $^1\text{H}$  NMR spectra were obtained with the Perkin Elmer R32B 90 MHz spectrometer using samples dissolved in  $\text{CDCl}_3$  containing 3% tetramethylsilane. Mass spectra (MS) and combined GLC-MS were obtained on a Finnigan Model 1015D chemical ionization mass spectrometer with a System Industries Model 150 control system. The gas chromatograph (Finnigan Model 9500) was operated with temperature programming (120–300 °C, 10 °C/min) and with helium at 30 mL/min

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**Figure 1.** Photochemical pathway of (1*RS*)-*trans*- and (1*RS*)-*cis*-permethrin to account for the various photoproducts obtained in the UV and sunlight studies. Also shown in the position of <sup>14</sup>C-labeling on the acid (ac\*) and alcohol (alc\*) portions of the permethrin molecule.

as the carrier gas. Isobutane was used as the reagent gas at a source pressure of 0.4 Torr.

**Photolysis Procedures.** *t*- or *c*-per in solution or in the solid phase was irradiated with UV light ( $\lambda > 290$  nm) or sunlight.

**UV Irradiation.** The individual isomers at 0.01 M in methanol or hexane were irradiated in Pyrex NMR tubes using a Rayonet reactor (The Southern N.E. Ultraviolet Co., Middletown, Conn.) and RPR 3000 lamps (peak output  $\lambda$  290–320 nm) with the tubes in a "merry-go-round" arrangement within the reactor insuring equal exposure of all samples. "Dark" samples were kept as controls. Product analysis involved GLC and GLC-MS in unlabeled studies and TLC in labeled studies.

The individual Ac\* and Alc\* preparations of *t*- and *c*-per at 0.1–0.2 ppm in 20 mL of water or water-acetone (49:1) mixture were irradiated for various times at  $\lambda > 290$  nm. Photolyzed samples were combined with several acetone washes of the reaction tube and then lyophilized to dryness. The residues were rinsed several times with ethyl acetate and acetone, and products in the combined rinses were analyzed by TLC cochromatography and LSC. For comparison, Alc\*-per and [<sup>14</sup>C]2,4-D at 0.05 ppm in water were photolyzed as above, followed by two-dimensional TLC for each of the sample times with the CFE solvent system utilized for both directions.

**Sunlight Photolysis on Soil.** The [<sup>14</sup>C]per preparations (8  $\mu$ g) were spotted on Dunkirk Silt Loam soil (organic matter, 2.6%; sand, 29.6%; silt, 56.4%; clay, 14.0%; pH 6.0) (provided by FMC Corp.) spread as a 0.25-mm thickness layer on 20  $\times$  20 cm glass plates. The plates were exposed to direct sunlight for 48 days or they were wrapped in aluminum foil before comparable exposure (controls). The average ambient temperature varied from a minimum of 15  $^{\circ}$ C at night to a maximum of 40  $^{\circ}$ C during the day. After exposure, the treated soil regions were scraped into vials containing 3 mL of methanol-ether (1:1) mixture. For extraction, each vial was placed in a sonicator for 15 min, the solvent decanted, this procedure repeated twice more, and the residue was then transferred to a sintered glass filter and washed several times with methanol. The extracts and washes

were combined for quantitation of an aliquot by LSC and analysis of the remainder by TLC. Unextractable <sup>14</sup>C was determined by combustion utilizing a Packard Tri-Carb Model 306 Sample Oxidizer.

**Sensitized Photooxidation.** A mixture of 0.1–0.5 g of *t*- or *c*-per or *t*-monochloro-per and Rose Bengal (0.1 g) in anhydrous methanol (600 mL) in a standard Hanovia apparatus (Conrad-Hanovia, Inc., Newark, N.J.) was irradiated with a 40-W G.E. Showcase lamp (General Electric Co., Cleveland, Ohio) for up to 7 days while oxygen was bubbled through the solution (for similar reaction conditions in a study on resmethrin, see Ueda et al., 1974). The reaction was monitored by GLC and TLC.

**Characterization of Photoproducts.** Labeled photoproducts were tentatively identified by TLC cochromatography with authentic standards in each of three solvent systems as shown in Table I. Unlabeled compounds in the solution photochemistry studies were characterized by GLC-MS, comparing the MS fragmentation patterns with standards (Table I).

## RESULTS

**Photodecomposition in Methanol and Hexane.** Both per isomers photodecompose slightly faster in hexane than in methanol, and in each solvent the *cis* isomer photodecomposes  $\sim 1.6$  times faster than the *trans* isomer (Table II). This photodecomposition is sensitized by PBald and benzophenone and is efficiently quenched by 1,3-cyclohexadiene.

The solution photochemistry of the per isomers involves extensive isomerization of the cyclopropane ring, i.e., interconversion of the *trans* and *cis* isomers (Figure 2). The isomerization rate increases in the order methanol < hexane < water. At equilibrium, the more thermodynamically stable *trans* isomer constitutes 65–70% of the isomer mixture.

A more complete analysis of the photolysis products in methanol solution is given in Table III. Although the results are tabulated only for the 4-h irradiation sample, the type of products observed throughout the reaction (0–4 h) does not change with only the relative amounts varying. Isomerization (*trans/cis*) is a significant process but the

Table I. Chromatographic Properties and Mass Spectral Data of [1*RS*]-*trans*- and [1*RS*]-*cis*-Permethrin, Their Photoproducts and Derivatives

Compound	TLC $R_f$			$m/e$ (rel intensity) <sup>a</sup>
	CBX2	BFE	CFE	
Permethrin and Other Esters				
Per				
Trans	0.59	0.75	0.72	393 (14.6), 392 (20.2), 391 (22.1), 390 (15.4), 358 (11.5), 357 (27.3), 356 (40.7), 355 (63.6), 354 (31.2), 185 (69.2), 184 (14.6), 183 (100).
Cis	0.72	0.75	0.74	393 (12.3), 392 (16.8), 391 (18.1), 390 (12.2), 356 (12.3), 355 (21.3), 354 (10.9), 185 (38.1), 184 (15.2), 183 (100).
Monochloro-per	0.54	0.75	0.64	360 (11.3), 359 (23.8), 358 (39.3), 357 (52.9), 356 (26.8), 340 (13.7), 339 (25.0), 315 (11.9), 313 (35.7), 311 (11.3), 199 (32.1), 185 (67.8), 184 (14.3), 183 (100), 129 (14.3).
3-Phenoxybenzyl dimethylacrylate	0.41	0.63	0.69	284 (10.6), 283 (57.9), 185 (49.6), 184 (15.6), 183 (100).
Products Derived from Acid Moiety				
Cl <sub>2</sub> CA				
Trans	0.00	0.40	0.28	213 (15.5), 211 (71.3), 209 (100).
Cis	0.00	0.47	0.38	213 (12.1), 211 (65.3), 209 (100), 113 (13.0).
Cl <sub>2</sub> CA methyl esters				
Trans	0.50	0.66	0.67	227 (10.3), 225 (62.6), 224 (10.5), 223 (100), 127 (20.3).
Cis	0.65	0.66	0.69	227 (10.8), 225 (64.5), 224 (11.1), 223 (100).
CICA				
Trans	0.00	0.39	0.28	177 (35.3), 176 (10.1), 175 (100), 139 (29.9).
Products Derived from Alcohol Moiety				
PBalc	0.04	0.37	0.36	186 (10.1), 185 (70.1), 184 (14.9), 183 (100).
PBald	0.36	0.58	0.65	200 (14.7), 199 (100), 185 (10.7).
PBacid	0.00	0.33	0.17	216 (13.6), 215 (100), 185 (19.1), 183 (29.6).
Benzyl alcohol	0.04	0.24	0.32	92 (10.4), 91 (100).
Benzaldehyde	0.23	0.54	0.61	108 (10.1), 107 (100).
Benzoic acid	0.00	0.30	0.22	124 (21.1), 123 (100), 105 (18.6).
3-HO-benzylalcohol	0.00	0.05	0.07	163 (25.7), 125 (14.8), 109 (34.1), 107 (100).
3-HO-benzaldehyde	0.00	0.26	0.34	124 (10.3), 123 (100).
3-HO-benzoic acid	0.00	0.10	0.06	140 (10.1), 139 (100).

<sup>a</sup> The CI-MS were recorded using isobutane as the reagent gas and ions with relative intensity <5% are not reported.

Table II. Photodecomposition of (1*RS*)-*trans*- and (1*RS*)-*cis*-Permethrin in Hexane and Methanol Solutions Using UV Light ( $\lambda > 290$  nm)

Solvent	Additive	$t_{1/2}$ , min <sup>a</sup>	
		Trans	Cis
Hexane	None	75	43
Methanol	None	92	58
Methanol	PBald <sup>b</sup>	87	46
Methanol	Benzophenone <sup>b</sup>	95	63
Methanol	1,3-Cyclohexadiene <sup>b</sup>	c	c

<sup>a</sup> The pseudo-first-order rate constant ( $k$ ) calculated from the initial stages of photolysis (0–30% reaction) is used in determining  $t_{1/2}$  ( $0.693/k$ ). <sup>b</sup> 50-fold molar excess. <sup>c</sup> No reaction.

major products are formed by ester cleavage reactions, i.e., >55% of the recovered <sup>14</sup>C detected using Ac\*-per is due to *t*-Cl<sub>2</sub>CA and *c*-Cl<sub>2</sub>CA and the corresponding methyl esters and from Alc\*-per is attributable to PBalc and its methyl ether. Trace amounts of monochloro-per are formed from both isomers of starting per. The stereochemistry of the monochloro-per was not determined due to the small amount and the lack of reference standards. Also observed with Alc\*-per are small amounts of PBald and PBacid. Each labeled material gives unidentified polar components. Although a quantitative study of the photoproducts in hexane was not carried out, the major products were identified by cochromatography and GLC-MS analysis as *t*- and *c*-Cl<sub>2</sub>CA and PBalc.

**Photodecomposition in Water and Water-Acetone Mixture.** The per isomers undergo extensive and relatively rapid isomerization and ester cleavage on photolysis in water or water-acetone (49:1) mixture, the reaction occurring more rapidly in the presence of acetone but yielding the same identified products under both conditions with the Ac\* and Alc\* preparations (Table IV).

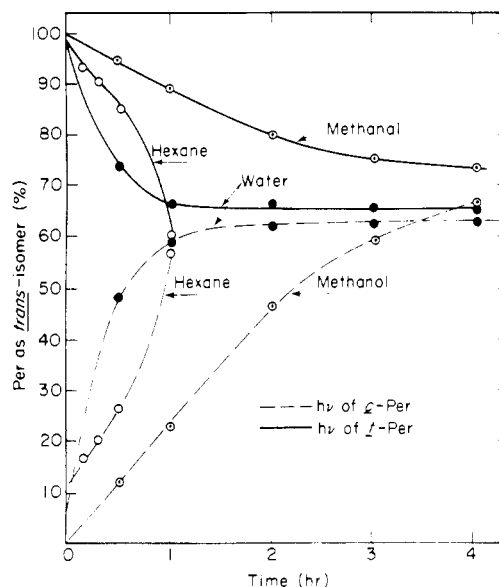


Figure 2. Relative isomerization rates leading to equilibrium *cis/trans* mixtures of (1*RS*)-*cis*- or (1*RS*)-*trans*-permethrin in methanol (O), hexane (O), and water (●).

Isomerization of the cyclopropane ring is a major reaction, reaching equilibrium in 3–4 h in water (Figure 2) and at >1 h in aqueous acetone. Other esters in trace amounts are monochloro-per and the dimethylacrylate (Table IV).

The acid moiety is liberated on photolysis to a greater extent in water than in water-acetone (49:1) and more of the Cl<sub>2</sub>CA undergoes isomerization within 1 h in the water reactions. Trace amounts of CICA are also detected.

The major identified photoproduct from the alcohol moiety is PBalc followed by 3-HO-benzyl alcohol and they are in smaller amounts in the water-acetone than in the

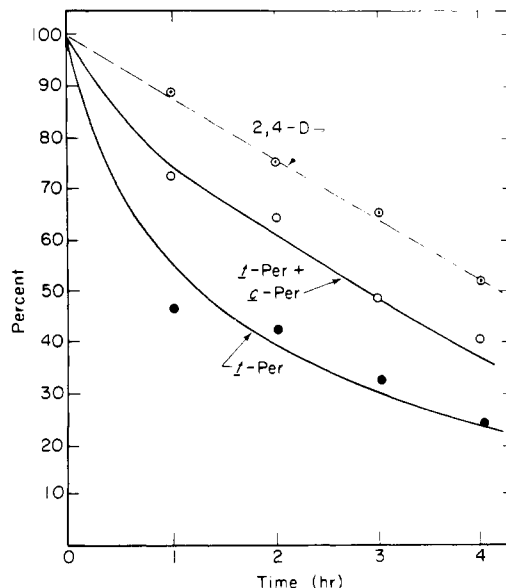
**Table III. Photoproducts of (1RS)-trans- and (1RS)-cis-Permethrin in Methanol Solution Following 4-h Irradiation Using UV Light ( $\lambda > 290$  nm)**

Compound	[ <sup>14</sup> C]Permethrin equivalents, %	
	Trans	Cis
Per and Photoproducts Retaining Ester Linkage		
Per		
Trans	20.6	17.5
Cis	7.3	9.1
Monochloro-per	0.3	0.4
Photoproducts Derived from Acid Moiety		
Cl <sub>2</sub> CA		
Trans	29.2	23.4
Cis	12.8	21.5
Cl <sub>2</sub> CA, methyl esters (Trans + cis)	10.7	10.3
Unknowns <sup>a</sup>	19.1	17.8
Photoproducts Derived from Alcohol Moiety		
PBalc, methyl ether	53.2	53.0
PBalc	2.8	2.5
PBacid	3.4	2.9
Unknowns <sup>b</sup>	12.4	14.6

<sup>a</sup> Six products detected with Ac\*-per isomers at *R<sub>f</sub>* 0.0-0.3 (BFE) and varying in amounts from 1.9-4.9% of the recovered <sup>14</sup>C. A portion of these products may be esters. <sup>b</sup> Nine products detected with alc\*-per isomers at *R<sub>f</sub>* 0.0-0.3 (BFE) and varying in amount from 2.0-4.3% of the recovered <sup>14</sup>C. A portion of these products may be esters.

water reactions (Table IV). Other products (>1%) are PBacid and benzoic acid and traces of PBald, benzyl alcohol, benzaldehyde, and 3-HO-benzoic acid.

Large amounts of polar material are detected in water from both isomers, labeled in either the Alc\* or Ac\* positions (Table IV). The polar products form faster in the presence of 2% acetone. With Ac\*-per at 4 h, two of the unknowns chromatograph below Cl<sub>2</sub>CA. They vary in amount from 1.1 to 6.5% of the <sup>14</sup>C, largest amount appearing at the origin. With Alc\*-per at 4 h, three of the unknowns (individually 1.1-2.4%) chromatograph (BFE) between PBalc and per and the remainder (5) (individually 1.9-11.8%) appear at *R<sub>f</sub>* 0.00-0.26 with the greatest amount at *R<sub>f</sub>* 0.00. The unknown polar products also



**Figure 3. Comparative photodecomposition of [1RS,trans]-permethrin and 2,4-D in water using UV light. Also shown is disappearance of total permethrin, i.e., the sum of starting *t*-per plus that isomerized to *c*-per during the reaction.**

appear, but in larger amounts, in the presence of acetone. It is not known if some or most of these products retain the ester linkage or are formed by ester cleavage reactions.

Photolysis of 2,4-D (comparison standard) in water occurs at an initial rate slightly slower than that of *t*-per (or of the mixture of *t*- and *c*-per formed during this photolysis) (Figure 3).

**Photodegradation on Soil.** Exposure of the per isomers on soil for 48 days results in ~55% loss in sunlight and ~35% loss in the dark (Table V). The amount of unextractable material is ~6% in the dark and ~18% in the light. Relatively little isomerization at the cyclopropane ring is encountered relative to the solution photochemistry studies but, as before, *c*-per is more extensively isomerized than *t*-per. Trace amounts of the esters, monochloro-per and the dimethylacrylate, are formed. There is relatively little difference in the amount

**Table IV. Photoproducts of (1RS)-trans- and (1RS)-cis-Permethrin in a Water and Water-Acetone (49:1) Mixture Using UV Light ( $\lambda > 290$  nm)**

Product	[ <sup>14</sup> C]Permethrin equivalents, % at indicated hour irradiation															
	Water								Water-acetone (49:1)							
	Trans				Cis				Trans				Cis			
	1	2	3	4	1	2	3	4	0.25	0.5	0.75	1	0.25	0.5	0.75	1
Permethrin and Photoproducts Retaining Ester Linkage																
Per																
Trans	48.2	43.7	29.7	25.4	41.2	38.0	29.1	25.5	77.8	68.3	53.5	41.8	17.6	25.0	25.8	25.7
Cis	25.5	21.9	15.3	15.1	32.8	26.0	18.6	16.0	6.8	10.2	11.5	12.5	67.0	53.1	42.5	30.9
Other esters <sup>a</sup>	0.6	0.7	0.9	0.9	0.5	0.5	0.8	0.9	0.4	0.8	0.8	1.0	0.5	0.7	0.7	0.9
Photoproducts Derived from Acid Moiety Only																
Cl <sub>2</sub> CA																
Trans	9.3	14.7	27.1	25.6	5.2	11.1	17.0	19.6	0.7	0.8	1.2	1.9		0.1	0.1	0.2
Cis	4.6	6.7	11.7	11.3	5.7	10.4	12.0	13.2	0.7	1.0	1.1	1.5	0.6	0.8	0.9	2.1
Unknowns <sup>b</sup>	11.8	12.3	15.3	21.7	14.6	14.0	22.5	24.8	13.6	18.9	31.9	41.3	14.3	20.3	30.0	40.2
Photoproducts Derived from Alcohol Moiety Only																
PBalc	11.4	12.3	18.3	22.8	9.5	10.9	19.6	20.4	1.7	4.5	9.6	12.0	4.2	4.6	7.6	10.4
PBacid	1.6	1.7	2.4	2.2	2.5	2.0	2.0	2.0	1.8	2.7	3.4	4.5	1.8	2.1	3.6	4.0
Benzoic acid	1.6	2.0	2.8	2.8	1.1	1.3	2.2	2.3	0.2	0.7	1.5	2.0	0.5	0.8	1.0	1.3
3-HO-Benzyl alcohol	3.4	5.1	6.5	7.8	2.0	2.9	4.8	6.4	0.4	0.8	1.0	2.5	0.4	0.7	0.8	1.4
Unknowns <sup>c</sup>	7.7	12.6	24.1	23.0	10.4	18.4	22.9	26.5	10.9	12.0	18.7	23.7	8.0	13.0	18.0	25.4

<sup>a</sup> Monochloro-per and the dimethylacrylate. <sup>b</sup> Additional products in minor amounts (0.2-0.4%) are the Cl<sub>2</sub>CA isomers. <sup>c</sup> Additional products in minor amounts (<0.3%) are PBald, 3-HO-benzoic acid, benzyl alcohol, and benzaldehyde.

Table V. Degradation Products of (1*RS*)-*trans*- and (1*RS*)-*cis*-Permethrin Following 48-Days Exposure in the Dark or to Sunlight on a Thin Layer of Soil

Compound or product	[ <sup>14</sup> C]Permethrin equivalents, %			
	Dark		Sunlight	
	Trans	Cis	Trans	Cis
Per and Products Retaining Ester Linkage				
Per				
Trans	49.9	0.4	14.2	0.9
Cis	0.3	49.2	0.4	15.8
Monochloro-per	0.0	0.0	0.1	0.2
3-Phenoxybenzyl dimethylacrylate	0.0	0.0	0.2	0.1
Products Derived from Acid Moiety Only				
Cl <sub>2</sub> CA				
Trans	2.7	0.1	0.5	0.3
Cis	0.2	3.4	0.3	1.8
Unknowns				
Extractable	2.3	3.1	5.6	6.2
Unextractable	8.4	5.4	13.7	9.9
Loss	36.2	38.4	65.0	64.8
Products Derived from Alcohol Moiety Only				
PBalc	4.8	4.8	3.7	4.1
PBacid	0.6	1.1	0.3	0.2
Others <sup>a</sup>	0.3	0.4	1.1	1.7
Unknowns				
Extractable	3.0	4.1	7.7	7.9
Unextractable	7.1	5.2	17.6	18.6
Loss	34.0	34.8	54.7	50.5

<sup>a</sup> Includes benzyl alcohol, benzoic acid, and 3-HO-benzyl alcohol. These products, although in trace amounts, are at higher levels in sunlight than in the dark.

of Cl<sub>2</sub>CA detected in the dark or light with either *t*- or *c*-per. PBalc is the major cleavage product of the alcohol moiety. Other products detected are essentially the same as those in the solution photolysis studies. Most of the unidentified extractable <sup>14</sup>C products give *R<sub>f</sub>* 0.00 and 0.30 (BFE) with the major portion at the origin.

Control experiments in which Alc\*- and Ac\*-per were applied to soil and held under ambient conditions for 6–8 h and worked up identically to those samples in Table V showed >98% <sup>14</sup>C recovery as per with <1% of the <sup>14</sup>C present as unextractable products.

**Resistance of Dichlorovinyl Moiety toward Epoxidation.** Per and monochloro-per do not undergo photooxidation or other reactions within 7 days in methanol in the presence of excess O<sub>2</sub> using Rose Bengal as a sensitizer. Per does not react with a tenfold molar excess of *m*-chloroperoxybenzoic acid or trifluoroperoxyacetic acid in dichloromethane solution at 25 °C. However, monochloro-per undergoes up to 10% reaction with the five-ten-fold molar excess of *m*-chloroperoxybenzoic acid under the same conditions with the major portion of the reaction products being polar, chlorine-containing unknowns and PBalc as determined by GLC-MS. A very minor reaction product isolated (0.2–0.6% of starting material) by chromatography on a Florisil column and preparative TLC (CBX2) was found to contain one chlorine atom and to give a parent ion of *m/e* 372 corresponding to monochloro-per plus 16. This product breaks down readily under acidic TLC conditions but is sufficiently stable for GLC analysis. MS gives *m/e* 183 as the base peak (phenoxybenzyl ion), indicating that the additional oxygen is on the acid portion of the molecule. Fourier transform-<sup>1</sup>H NMR of the isolated material shows essentially the same absorption pattern as the starting monochloro-per except that the vinyl protons between δ 5.3–6.4 ppm are absent and an additional absorption appears corresponding to one proton at 3.60 ppm. This evidence suggests that the epoxide of monochloro-per

may form under extreme reaction conditions with an excess of oxidant.

## DISCUSSION

Figure 1 shows a photodecomposition scheme for *t*- and *c*-per consistent with the findings under all exposure conditions except in methanol where major products are the methyl esters of Cl<sub>2</sub>CA and the methyl ether of PBalc. Two major reactions are involved in each case, isomerization of the cyclopropane ring and ester cleavage before or after isomerization. At equilibrium, the more thermodynamically stable *trans* isomer always predominates. Photoisomerization probably occurs via a triplet energy state, i.e., it proceeds in the presence of excess PBald and benzophenone which act as photosensitizers and is efficiently quenched by 1,3-cyclohexadiene. Minor photolysis pathways lead to monochloro-per, the dimethylacrylate and ClCA. The liberated alcohol moiety is oxidized to the aldehyde and carboxylic acid and undergoes minor cleavage of the ether linkage, with or without retention of the phenolic hydroxyl on the fragments obtained. Cleavage of the diphenyl ether group could also occur within per prior to ester cleavage.

The per isomers rapidly photodecompose on irradiation with UV light (λ >290 nm) in hexane or methanol solution or in aqueous medium, solvents of widely varying polarity. Relatively large amounts of unidentified polar products are formed in each case, possibly from opening of the cyclopropane ring. These materials are in particularly high amounts in the water-acetone mixture where they may result from further photodecomposition of the initial products with excess acetone. Alternatively, the degradation process may just be more extensive due to the high triplet energy (78 kcal/mol) of acetone being transmitted to other portions of the molecule besides the carbonyl group. Evidence for this latter possibility comes from the greater *cis/trans* isomerization of the *cis* isomer in water alone.

*t*- and *c*-per degrade slowly on soil in the dark or when exposed to sunlight. There is relatively little isomerization of the cyclopropane ring; this may result from the predominance of other reactions proceeding in the solid phase as compared to those in solution (Watkins, 1974). Volatility, or more likely microbial degradation (Kaufman et al., 1977), appears to play a large role in the residue loss. The lack of a large difference in the amount of Cl<sub>2</sub>CA in the dark and sunlight suggests that the ester cleavage reaction on soil is largely chemical rather than photochemical or that the liberated Cl<sub>2</sub>CA undergoes more rapid breakdown in the light than in the dark. However, in sunlight there are larger amounts of PBalc and polar unknowns. These findings suggest that the initial cleavage products formed chemically or photochemically are further degraded, this occurring more rapidly with Cl<sub>2</sub>CA than with PBalc.

Photoproducts that retain the ester linkage appear in only minor amounts, except those from cyclopropane isomerization. Trace amounts of monochloro-per are detected, but this compound is very resistant to epoxidation. Chlorine atoms and other halogens (Ruzo et al., 1977) at the vinyl position have a pronounced effect in protecting this substituent from oxidation or epoxidation as compared to the isobutenyl substituent in chrysanthenates.

## LITERATURE CITED

- Elliott, M., Farnham, A. W., Janes, N. F., Needham, P. H., Pulman, D. A., Stevenson, J. H., *Nature (London)* **246**, 169 (1973).  
Elliott, M., *ACS Symp. Ser.* **42**, 1 (1977).

- Elliott, M., Janes, N. F., in "Pyrethrum the National Insecticide", Casida, J. E., Ed., Academic Press, New York, N.Y., 1973, p 84.
- Holmstead, R. L., Casida, J. E., Ruzo, L. O., *ACS Symp. Ser.* **42**, 137 (1977).
- Kaufman, D. D., Haynes, S. C., Jordan, E. G., Kayser, A. J., *ACS Symp. Ser.* **42**, 147 (1977).
- 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).

Watkins, D. A. M., *Chem. Ind.*, 185 (1974).

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## Degradation of Methabenzthiazuron in the Soil

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The degradation of methabenzthiazuron [*N*-(2-benzothiazolyl)-*N,N'*-dimethylurea or MBT] in the soil was examined by comparing the rates of  $^{14}\text{C}$  evolution from soils amended with specifically  $^{14}\text{C}$ -labeled MBT and related compounds. It was found that the heterocyclic moiety of MBT degraded slowly to  $\text{CO}_2$  and the urea side chain provided additional stability to the molecule. Both *N*-(2-benzothiazolyl)methylamine and benzothiazolone degraded more rapidly than MBT, thus they would not likely be stable intermediate metabolites of MBT degradation. Also, both of the methyl groups on the urea moiety demethylated readily. However, the carbonyl carbon on the urea moiety degraded to  $\text{CO}_2$  at rates comparable to those of the heterocyclic carbons, indicating that stable intermediate metabolites of MBT would contain a partially degraded urea moiety together with the heterocyclic moiety.

Methabenzthiazuron or MBT [*N*-(2-benzothiazolyl)-*N,N'*-dimethylurea] is the active ingredient of the herbicide Tribunil, which controls a broad spectrum of weeds in cereal crops (Hack, 1969). Its effectiveness persists in the field soil for more than one growing season (Becker and Plüghan, 1969; Führ and Mittelstaedt, 1976). However, little is known about the nature of its persistence or about the possible pathways of its degradation in the soil. Pont et al. (1974) reported that MBT was taken up by plants in hydroponic culture and transformed to a hydroxyl-methyl derivative before it was demethylated or conjugated with plant constituents. Demethylation of the 3-methyl group of MBT by fungi was reported by Wallnöfer et al. (1976) and that of the 1-methyl group in the soil was confirmed by Mittelstaedt et al. (1977). The objective of this study was to elucidate the processes involved in the soil degradation of MBT by comparing the rates of  $^{14}\text{C}$  evolution during soil incubation with MBT and various related compounds which were labeled with  $^{14}\text{C}$  at specific positions on the molecules. By using the radiotracer techniques, both the degradation rates and possible degradation pathways could be evaluated.

### MATERIALS AND METHODS

**Chemicals.** Reagent grade and  $^{14}\text{C}$ -labeled experimental chemicals were synthesized and supplied by courtesy of Bayer AG. These included: (benzene-ring- $^{14}\text{C}$ )-, (benzothiazolyl-2- $^{14}\text{C}$ )-, (methyl-1- $^{14}\text{C}$ )-, (methyl-3- $^{14}\text{C}$ )-, and (carbonyl- $^{14}\text{C}$ )-labeled MBT; (benzene-ring- $^{14}\text{C}$ )-labeled benzthiazuron and benzothiazolyl-

amine; (benzothiazolyl-2- $^{14}\text{C}$ )-labeled benzothiazolylamine, benzothiazolone, and *N*-(2-benzothiazolyl)methylamine; and *N*-(2-benzothiazolyl)[ $^{14}\text{C}$ ]methylamine. A list of these chemicals showing their structural formulae is given in Table I.

**Soils.** Two soils, a Laacherhof sandy loam and a Walbeck humic sand, were used in these studies. Some of the physical and chemical properties of these soils are summarized in Table II.

**Degradation Study.** The basic procedure used for studying degradation rates was to monitor the rates of  $^{14}\text{C}$  evolution during incubation of soils amended with  $^{14}\text{C}$ -labeled chemicals under controlled temperature, aeration, and moisture conditions. Each soil sample was treated with a  $^{14}\text{C}$ -labeled chemical, moistened to 65% of the soil water-holding capacity, and incubated in a closed Erlenmeyer flask in a water bath maintained at 24 °C. The flask was wrapped in black plastic bags to darken the soil environment and aerated by a stream of moist  $\text{CO}_2$ -free air which also swept the  $\text{CO}_2$  evolved from the soil out of the flask, through a scrubbing tower containing concentrated  $\text{H}_2\text{SO}_4$ , and into a 1 N NaOH absorbing solution. The NaOH solution was changed periodically and its radioactivity was measured in a Tri-Carb Liquid Scintillation Spectrometer using 4 mL of the NaOH solution and 15 mL of Insta-Gel liquid scintillation cocktail (Packard Instrument Co.). Counting efficiencies were corrected by the channels-ratio method. The amount of radioactivity found in the NaOH solution was taken as a measure of the degree of degradation of the  $^{14}\text{C}$ -labeled chemical and was expressed as a percentage of the total radioactivity applied to the soil.

**Methods for Extraction and Analysis.** Extraction of MBT and its metabolites from the soil was based on the procedure of Cheng and Führ (1976). The components in the soil extracts were separated and identified by thin-layer chromatography or by column chromatography followed by gas chromatography (Pont et al., 1974; Jarczyk, 1972)

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