

4 min and the material was not detectable after 15 min of irradiation. In methanol, dimethylfuran reacts with singlet dioxygen to form an ozonide-like peroxide which undergoes solvolysis to form a hydroperoxide (Foote and Wexler, 1964).

Photochemical oxidations taking place in aqueous solutions of organic dyes, so-called sensitizers, are frequently attributed to the presence of singlet oxygen (Acher and Dunkelblum, 1979; Larson and Stabler, 1978). Thiobencarb, however, is a very poor singlet oxygen acceptor. This might be anticipated as singlet oxygen is known to be a relatively selective oxidant, reacting primarily with sulfides and certain olefins. In similar experiments, phosphorodithioates (malathion), phosphorothioates (ethyl and methyl parathion), and other thiocarbamates (molinat and drepamon) proved unreactive to photochemically generated singlet oxygen (Draper, 1979). Of the agricultural chemicals examined, only disulfoton reacted with singlet oxygen due to the presence of an ethylthioethyl sulfide moiety.

#### CONCLUSION

Free radical reactions are of major importance in indirect photolysis processes in water. The photooxidations observed in aqueous hydrogen peroxide, methylene blue, and tryptophan are similar to those produced by Fenton's reagent, supporting the view that hydrogen peroxide and hydroxyl radicals are the active oxidizing species in each of these systems. Thiobencarb is not oxidized by singlet molecular oxygen.

This work emphasizes the differences between sensitized photooxidations in organic media and those in water. A triplet dye, for example, may exhibit only singlet oxygen reactions in a low dielectric medium, while in water free radical reactions, due to the formation of peroxide, become important. Many photooxidation reactions previously ascribed to the presence of singlet oxygen in water may be due to hydroxyl radical. A requirement for oxygen or the demonstrated reactivity with a known singlet oxygen

acceptor will not distinguish these mechanisms.

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#### LITERATURE CITED

- Acher, A. J.; Dunkelblum, E. *J. Agric. Food Chem.* **1979**, *27*, 1164.  
 Blinn, R. C. *J. Assoc. Off. Anal. Chem.* **1964**, *47*, 641.  
 Casida, J. E.; Kimmel, E. C.; Ohkawa, H.; Ohkawa, R. *Pestic. Biochem. Physiol.* **1975**, *5*, 1.  
 Cowan, D. O.; Drisko, R. L. "Elements of Organic Photochemistry"; Plenum: New York, 1976; p 75.  
 Crosby, D. G.; Wong, A. S. *J. Agric. Food Chem.* **1973**, *21*, 1052.  
 Draper, W. M. M.S. Thesis, University of California, Davis, CA, 1977.  
 Draper, W. M. Ph.D. Dissertation, University of California, Davis, CA, 1979.  
 Fendler, J. H.; Gasowski, G. L. *J. Org. Chem.* **1968**, *33*, 1865.  
 Foote, C. S.; Wexler, S. *J. Am. Chem. Soc.* **1964**, *86*, 3879.  
 Gollnick, K. *Adv. Photochem.* **1968**, *6*, 1.  
 Heidt, L. *J. Sol. Energy* **1967**, *11*, 123.  
 Ishikawa, K.; Nakamura, Y.; Kuwatsuka, S. *Nippon Noyaku Gakkaishi* **1976**, *1*, 49.  
 Karger, B. L.; Snyder, L. R.; Horvath, C. "An Introduction to Separation Science"; Wiley: New York, 1973; p 391.  
 Larson, R. A.; Stabler, P. P. *J. Environ. Sci. Health, Part A* **1978**, *A13*, 545.  
 McCormick, J. P.; Fischer, J. R.; Pachlatko, J. P.; Eisenstark, A. *Science (Washington, D.C.)* **1976**, *191*, 468.  
 McCormick, J. P.; Thomason, T. *J. Am. Chem. Soc.* **1978**, *100*, 312.  
 Merkel, P. B.; Kearns, D. R. *J. Am. Chem. Soc.* **1972**, *94*, 7244.  
 Randerath, K. "Thin-Layer Chromatography"; Academic Press: New York, 1964.  
 Snook, M. E.; Hamilton, G. A. *J. Am. Chem. Soc.* **1974**, *96*, 860.  
 Volman, D. H. *Adv. Photochem.* **1963**, *1*, 43.  
 Walling, C. *Acc. Chem. Res.* **1975**, *8*, 125.  
 Zepp, R. G.; Cline, D. M. *Environ. Sci. Technol.* **1977**, *11*, 359.

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## Pyrethroid Photochemistry: (*S*)- $\alpha$ -Cyano-3-phenoxybenzyl *cis*-(1*R*,3*R*,1'*R* or *S*)-3-(1',2'-Dibromo-2',2'-dihaloethyl)-2,2-dimethylcyclopropanecarboxylates

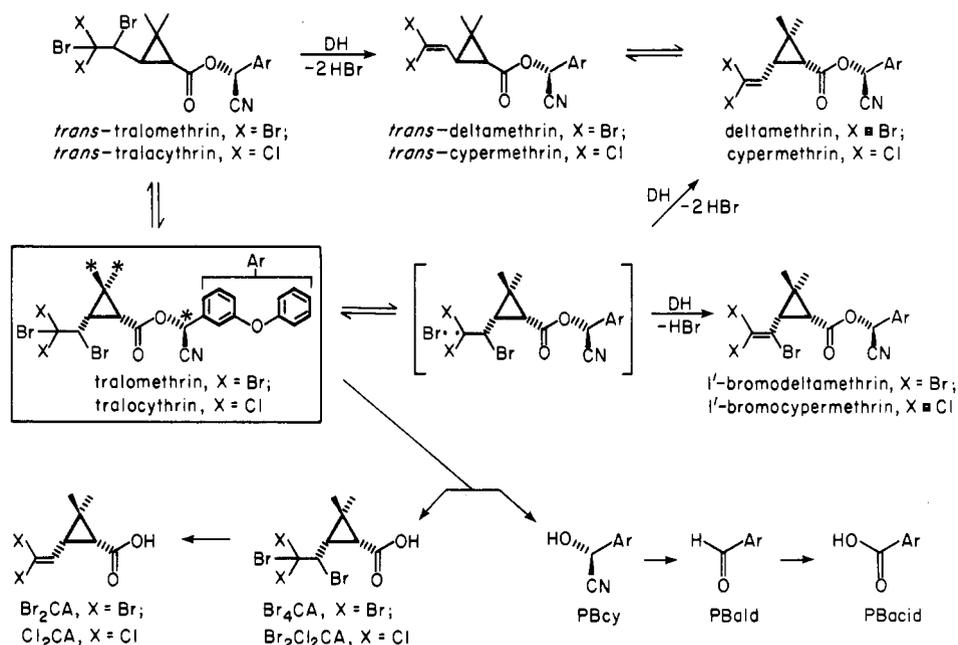
Luis O. Ruzo\* and John E. Casida

The *cis*-(1*R*,3*R*,1'*R* or *S*)-3-(1',2'-dibromo-2',2'-dihaloethyl)-2,2-dimethylcyclopropanecarboxylates, tralomethrin and tralocythrin (Roussel-Uclaf, proposed common names), readily debrominate when solutions or thin films are irradiated at 360 nm or by sunlight. Debromination results from homolytic cleavage of a carbon-bromine bond, followed by collapse of the resulting trihaloethyl radical to the dihaloalkene. Effects of various hydrogen donors and of triethylamine on the reaction rate and product distribution suggest that bromine is not produced from a concerted process. Dehydrobromination, 1*R*,*cis*  $\rightarrow$  1*RS*,*cis*,*trans* isomerization, and ester cleavage are also significant photochemical reactions of tralomethrin and tralocythrin in the solid phase whereas only the first two of these processes are important with irradiated solutions. The reactions of tralomethrin in solution are sensitized by triplet donors but the excited state responsible for debromination is not established.

The photochemical reactions of tralomethrin and tralocythrin (Figure 1) are of interest because these *cis*-(1*R*,3*R*,1'*RS*)-3-(1',2'-dibromo-2',2'-dihaloethyl)-2,2-di-

methylcyclopropanecarboxylates have remarkably high insecticidal potency (Ackermann et al., 1980; Roussel-Uclaf, 1978). Photoreactions of polyhalogenated alkyls usually involve dehydrohalogenation and reductive dehalogenation (Sammes, 1973). Photodehalogenation of vicinal dihalides yields alkenes by extrusion of two halogen atoms (Chapman et al., 1976; Huyser and DeMott, 1963) or molecular halogen (Yuan and Wijnen, 1980). The

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**Figure 1.** Major photodecomposition pathways for tralomethrin and tralocythrin in the presence of a hydrogen donor (DH). Compound designations and <sup>14</sup>C-labeling positions are also given. Although enantiomers were not separately analyzed, the indicated structures of photoproducts are those most likely to be formed, i.e., retention of configuration at cyclopropyl and benzyl carbons on debromination, dehydrobromination, and ester cleavage reactions and formation of 1*RS*,*cis*,*trans* mixtures on cyclopropane isomerization.

primary step in these reactions is homolytic cleavage of a carbon-halogen bond following  $n \rightarrow \sigma^*$  excitation.

Tralomethrin and tralocythrin contain 1',2'-dibromo-2',2'-dihaloethyl substituents replacing the 2',2'-dibromovinyl or 2',2'-dichlorovinyl substituents of deltamethrin (deca-methrin, NRDC 161) and the *cis*-(1*R*,3*R*), $\alpha$ *S* isomer of cypermethrin (NRDC 182), respectively (Figure 1) (Elliott and Janes, 1978). The photoreactivity of deltamethrin and related compounds is centered primarily in the acid moiety and involves 1*R*,*cis*  $\rightarrow$  1*RS*,*cis*,*trans* isomerization and reductive dehalogenation (Ru-zo and Casida, 1980; Ru-zo et al., 1976). The dihalovinyl substituent extends the conjugated system across the cyclopropane ring and thereby influences the pathways available for reaction. Tralomethrin and tralocythrin lack this unsaturated substituent so it is important to study their behavior under ultraviolet (UV) and sunlight irradiation.

#### MATERIALS AND METHODS

**Chemicals.** The compounds are designated as shown in Figure 1. Tralomethrin, tralocythrin, deltamethrin, and cypermethrin were used as *cis*-(1*R*,3*R*), $\alpha$ *S* compounds supplied by Roussel-Uclaf (Paris, France), who also provided the corresponding acid moieties (Br<sub>4</sub>CA; Br<sub>2</sub>Cl<sub>2</sub>CA; Br<sub>2</sub>CA; Cl<sub>2</sub>CA). Tralomethrin and tralocythrin with <sup>14</sup>C labeling (58.3 mCi/mmol) at either the methyl or the benzyl carbons were also donated by Roussel-Uclaf. The 1'*R* and 1'*S* isomers of each of tralomethrin and tralocythrin were separated by thin-layer chromatography (TLC) using hexane-ether (10:1) for development. Only the less polar isomer of tralomethrin (*R*<sub>f</sub> 0.28; presumably 1'*S*) and tralocythrin (*R*<sub>f</sub> 0.31; 1'*S*; Ackermann et al., 1980) was used in further studies since, at least in the latter case, the 1'*S* and 1'*R* isomers are similar in insecticidal activity (Ackermann et al., 1980). The 1*RS*,*trans*, $\alpha$ *S* isomers of tralomethrin and tralocythrin were prepared by bromination in carbon tetrachloride of the 1*RS*,*trans*, $\alpha$ *S* isomers of deltamethrin and cypermethrin ( $\alpha$ *RS* isomers from Roussel-Uclaf separated by TLC according to Ru-zo et al., 1977); they were characterized by chemical ionization mass spectrometry (CIMS), revealing spectra essentially iden-

tical with those of the *cis* isomers: *trans*-tralomethrin, 582 (M - Br), 503 (M - 2Br), 437; *trans*-tralocythrin: 574 (M + 1), 494 (M - Br), 349. Other unlabeled materials used as authentic standards for TLC and high-pressure liquid chromatography (HPLC) are previously described (Holmstead et al., 1978a; Ru-zo et al., 1977).

The dehydrobrominated compounds 1'-bromodeltamethrin and -cypermethrin (Figure 1) were prepared by first dehydrobrominating Br<sub>4</sub>CA and Br<sub>2</sub>Cl<sub>2</sub>CA on treatment with equimolar, 1,5-diazabicyclo[4.3.0]non-5-ene in dry tetrahydrofuran at 20 °C for 1 h. Addition of water and extraction of the reaction mixture with ether yielded the trihaloacids in >90% yield. Recrystallization from hexane gave materials with the following characteristics: 1'-bromo-Br<sub>2</sub>CA (mp 125-127 °C), 375 (M + 1, 13%), 295 (M - Br, 10%), 215 (9%); 1'-bromo-Cl<sub>2</sub>CA (mp 107-109 °C), 287 (M + 1, 15%), 251 (M - Cl, 3%), 207 (M - Br, 11%). The trihaloacids were reacted with excess thionyl chloride in benzene at reflux (2 h), and, after evaporation of the reagent, the resulting acid chlorides were coupled with  $\alpha$ -cyano-3-phenoxybenzyl alcohol in benzene containing equimolar pyridine. The trihaloesters (1'-bromodeltamethrin and 1'-bromocypermethrin) as  $\alpha$ *RS* mixtures were isolated by preparative TLC (HE solvent system, Table I) in 80% yield. They were characterized by nuclear magnetic resonance (NMR) spectroscopy which showed loss of the  $\delta$  6.18 and 6.69 signals associated with the C-1' proton in the spectra of deltamethrin and cypermethrin, respectively (Ru-zo et al., 1977). Their characteristic CIMS signals are as follows: 1'-bromodeltamethrin, 582 (M + 1, 38%), 357 (C<sub>8</sub>H<sub>8</sub>Br<sub>3</sub>O, 8%); 1'-bromocypermethrin, 494 (M + 1, 21%), 269 (C<sub>8</sub>H<sub>8</sub>Cl<sub>2</sub>BrO, 18%).

**Chromatography and Analyses.** HPLC utilized a Waters Associates Model 440 instrument equipped with an ultraviolet absorbance detector (254 nm) with the chromatographic conditions given in Table I. TLC utilized silica gel 60 F254 chromatoplates with 0.25-mm gel thickness (EM Laboratories, Elmsford, NY) developed as indicated in Table I. The ester cleavage products were chromatographed as previously described (Ru-zo et al., 1977). Photoproducts were detected by autoradiography

Table I. Chromatographic Properties of Tralomethrin, Traloccythrin, and Some of Their Derivatives and Isomers

compound (1 <i>R</i> , $\alpha$ <i>S</i> isomers)	HPLC, $R_t^a$	TLC, $R_f^b$	
		CT	HE
tralomethrin <sup>c</sup>	14.5 (13.2) <sup>d</sup>	0.44 (0.48) <sup>d</sup>	0.50 (0.51) <sup>d</sup>
<i>trans</i> - tralomethrin <sup>c</sup>	22.9 (20.9)	0.22 (0.24)	0.40 (0.42)
1'-bromo- deltamethrin	28.5 (26.0)	0.27 (0.29)	0.45 (0.47)
deltamethrin	19.2 (18.6)	0.31 (0.33)	0.53 (0.58)
<i>trans</i> - deltamethrin	25.7 (22.9)	0.29 (0.32)	0.48 (0.51)

<sup>a</sup> Retention times (minutes) on elution through a  $\mu$ Porasil column (30 cm  $\times$  3.9 mm i.d.) with chloroform-hexane (1:1) at a flow rate of 1 mL/min. <sup>b</sup> Silica gel chromatoplates developed twice in the first dimension with carbon tetrachloride-toluene (1:1) (CT) followed by twice in the second dimension with hexane-ether (4:1) (HE). <sup>c</sup> The less polar of the 1'*R* and 1'*S* isomers was used. <sup>d</sup>  $R_t$  and  $R_f$  values for corresponding traloccythrin derivatives are given in parentheses.

or in the case of unlabeled materials by their quenching of gel fluorescence at 254 nm. TLC regions were extracted with ether and aliquots quantitated by liquid scintillation counting.

**Spectroscopy.** NMR spectra were obtained with a Perkin-Elmer R32B 90-MHz instrument equipped with a Nicolet Model 1080 Fourier-Transform computer. Samples were dissolved in chloroform-*d* containing 1% tetramethylsilane as the internal standard. CIMS utilized a Finnigan Model 1015D spectrometer coupled with a System Industries Model 150 computer. A Finnigan 9500 gas chromatograph (GC) was interfaced with the mass spectrometer and equipped with a 3% dexyl on Varaport 30 (80-100-mesh) glass column (2 m  $\times$  3 mm i.d.) with a nitrogen flow of 20 mL/min programmed from 60 to 200 °C. Methane was the ionizing gas (900  $\mu$ m), and electron energies of 30 and 70 eV were used for esters and nonesters, respectively. Mass fragments above 600 amu were not detected.

**Irradiation Procedures.** Samples dissolved in spectroquality solvents (1 mL) were held in a "merry-go-round" arrangement during photolyses (0.5-3 h) in a Rayonet reactor equipped with RPR 2500 or 3600 lamps (The Southern New England Ultraviolet Co., Middletown, CT). Quartz or borosilicate glass tubes were utilized, and the samples were irradiated as duplicates ( $10^{-3}$  M unless indicated otherwise), each containing either [<sup>14</sup>C]methyl or -benzyl-labeled material. Solid-phase photolyses involved irradiating thin films (0.1 mg/cm<sup>2</sup>) at 360 nm (1 h) or with sunlight (5 h).

Ester photoproducts were tentatively identified by both TLC and HPLC cochromatography (Table I) and PBcy by TLC cochromatography of <sup>14</sup>C-labeled materials with authentic standards. CIMS was also used for photoproduct

characterization, directly for esters and following GC for PBald and the methyl esters of Cl<sub>2</sub>CA, Br<sub>2</sub>CA, and PBacid.

## RESULTS

**Direct Photolyses in Solution (360 nm).** *Photoproducts.* The UV absorption spectra of tralomethrin and traloccythrin are essentially identical and very similar to those of the dihalovinyl materials (Ruza et al., 1977). Tralomethrin photoproduct yields are summarized in Table II. Traloccythrin gives analogous products but reacts ~3-fold slower than tralomethrin. The photoproduct mixtures from reactions in methanol and 2-propanol reveal the occurrence in each case of debromination to deltamethrin and cypermethrin, dehydrobromination to 1'-bromodeltamethrin and -cypermethrin, and 1*R*,*cis*  $\rightarrow$  1*R*,*cis*,*trans* isomerization; there is also a small amount of ester cleavage products identical with those in solid-phase irradiations (Table III). Additional secondary radical reactions are predominant in benzene and cyclohexane, i.e., solvents which do not contain hydrogen readily abstractable by bromine radicals.

*Debromination and Dehydrobromination.* Short-term irradiation (<5% conversion) of tralomethrin in benzene yields deltamethrin as the major product (82%), while longer irradiation times result in a decrease in the amount of deltamethrin detected, accompanied by an increase in polar or polymeric products. At low tralomethrin concentrations (e.g.,  $10^{-5}$  M), this effect is minimized and deltamethrin is the major product. The reaction in methanol or 2-propanol proceeds at a somewhat slower rate, and the predominant product formed is deltamethrin, independent of concentration or extent of reaction. Introduction of isopropylbenzene (Table II) or toluene in the solution minimizes the secondary reactions and leads instead to a distribution of products resembling that obtained in alcohol solvent. 2,4,6-Tri-*tert*-butylphenol ( $10^{-2}$  M), an efficient radical scavenger, also increases the yield of deltamethrin without forming detectable reductively debrominated or coupled products. The presence of triethylamine considerably increases the reaction rate and deltamethrin yield (Table II). Photolysis of tralomethrin proceeds nearly twice as fast in chloroform as in chloroform-*d*, but the photoproduct distribution is not affected and is essentially identical with that in methanol.

When tralomethrin is irradiated in the presence of increasing concentrations of 1,3-cyclohexadiene, the reaction rate and debromination yields are enhanced, while formation of 1'-bromodeltamethrin and unidentified polar products is decreased (Figure 2). GC-CIMS reveals that a monobrominated cyclohexadiene [159 (M + 1)] is formed in this reaction. The yields of 1'-bromodeltamethrin and unidentified products resulting from the reactions of Br are thus minimized.

*1*R*,*Cis*  $\rightarrow$  1*R*,*Cis*,*trans* Isomerization.* *trans*-Deltamethrin is formed in substantial yields (Table II). A trace

Table II. Ester Photoproducts of Tralomethrin at  $10^{-3}$  M in Solution on 2-h Direct Irradiation at 360 nm

solvent or additive	% reacted	yield, % <sup>a</sup>		
		deltamethrin	1'-bromo- deltamethrin	<i>trans</i> - deltamethrin
methanol	34.3	62.2	3.6	11.7
2-propanol	32.5	63.6	3.2	12.5
benzene	42.8 <sup>b</sup>	8.6	5.2	1.5
	(22.1) <sup>c</sup>	(67.0)	(4.1)	(11.6)
isopropylbenzene (5% in benzene) <sup>d</sup>	37.9	74.9	4.0	9.5
triethylamine ( $10^{-3}$ M in benzene)	71.8	81.7	3.0	9.3

<sup>a</sup> Yields are expressed as percent of total product formation, i.e., percent of tralomethrin reacted. <sup>b</sup> Similar results were obtained in cyclohexane. <sup>c</sup> Tralomethrin at  $10^{-5}$  M. <sup>d</sup> Similar results were obtained on replacing isopropylbenzene with toluene.

Table III. Photoproducts of Tralomethrin and Tralocythrin in the Solid Phase under Sunlight and Ultraviolet Irradiation

tralomethrin <sup>a</sup>			tralocythrin <sup>b</sup>		
products	yield, % <sup>c</sup>		products	yield, % <sup>c</sup>	
	sun	UV		sun	UV
Esters					
deltamethrin	38.4	46.1	cypermethrin	48.4	68.0
1'-bromodeltamethrin	6.5	10.2	1'-bromocypermethrin	4.0	4.7
<i>trans</i> -tralomethrin	9.2	13.8	<i>trans</i> -tralocythrin	11.9	9.2
<i>trans</i> -deltamethrin	9.7	2.5	<i>trans</i> -cypermethrin	11.6	2.2
Ester Cleavage Products					
Br <sub>4</sub> CA	4.2	5.0	Br <sub>2</sub> Cl <sub>2</sub> CA	3.2	4.1
Br <sub>2</sub> CA	5.4	4.2	Cl <sub>2</sub> CA	3.9	4.1
PBcy	2.2	3.5	PBcy	1.9	1.2
PBald	3.1	1.5	PBald	4.1	2.6
PBacid	6.0	6.0	PBacid	2.0	2.9
Unknowns					
acid moiety	26.6	18.2	acid moiety	17.0	7.7
alc moiety	24.9	16.4	alc moiety	16.1	9.2

<sup>a</sup> Reacted tralomethrin was 24.3% on 5-h sunlight irradiation and 29.8% on 1-h UV irradiation. <sup>b</sup> Reacted tralocythrin was 13.3% on 5-h sunlight irradiation and 8.0% on 1-h UV irradiation. <sup>c</sup> Yields are expressed as percent of total product formation, i.e., percent of tralomethrin or tralocythrin reacted.

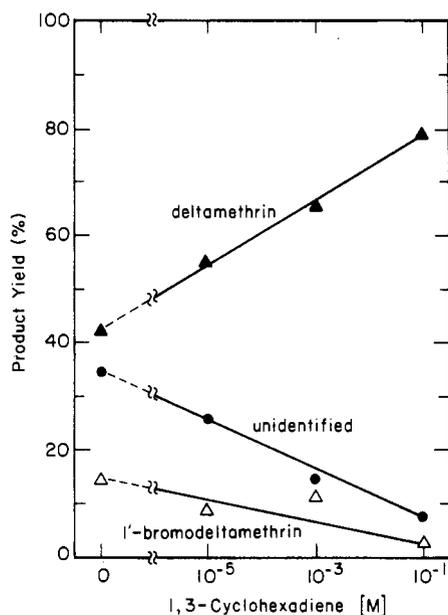


Figure 2. Photoproducts of tralomethrin at  $5 \times 10^{-4}$  M in benzene solution in the presence of 1,3-cyclohexadiene on 0.5-h direct irradiation at 360 nm. The results with  $10^{-6}$  M 1,3-cyclohexadiene were identical with those observed without an H donor. *Trans* isomers are not included. A semilog plot is used for convenience.

amount (<1%) of *trans*-tralomethrin was detected on irradiation of methanol solutions but not in the other systems. *trans*-Tralocythrin was not observed. In these reactions a small amount (0.5%) of  $\alpha$ -cyano-3-phenoxybenzyl dimethylacrylate (Ruzo et al., 1977) was detected from tralomethrin but not from tralocythrin.

**Ester Cleavage Reactions.** In every case there was some ester cleavage (2–5%) upon photolysis of tralomethrin and tralocythrin. The products (Figure 1) included some of those obtained from deltamethrin at comparable wavelengths (Ruzo et al., 1977), namely, Br<sub>2</sub>CA, PBcy, PBald, and PBacid. Many secondary products were obtained in benzene, of which 5–10% reacted with diazomethane to give substance(s) purified by TLC using the CT solvent system (Table I); the mass spectrum of this material revealed high molecular weight fragments ( $m/e$  471, 491, and 501) containing four bromine atoms. These compounds are probably polymers but remain unidentified.

**Energy Transfer Reactions.** Saturation of the solvent with either oxygen or nitrogen did not have a significant effect on the reaction rate or product distribution. Photolysis of tralomethrin in acetone gave deltamethrin (81%) and *trans*-deltamethrin (4%). Similar product distribution was obtained with benzophenone ( $E_t = 69$  kcal/mol) at 360 nm. Biphenyl ( $E_t = 65$  kcal/mol) and naphthalene ( $E_t = 60$  kcal/mol) at 254 nm sensitized the debromination and 1*R*,*cis* → 1*RS*,*cis*,*trans* isomerization efficiently but not the dehydrobromination reaction. 1,3-Cyclohexadiene did not quench but instead enhanced the rates of reaction and debromination (Figure 2).

**Photodecomposition in the Solid Phase.** Tralomethrin and tralocythrin yield similar products when irradiated as thin films on glass (Table III) as they do in solution (Table II). Tralocythrin degrades at a slower rate than tralomethrin in a manner analogous to that reported for cypermethrin relative to deltamethrin (Ruzo and Casida, 1980). Yields of *trans*-tralomethrin and -tralocythrin are greater in the solid phase than in solution. Debromination and dehydrobromination yields are greater upon UV irradiation than under sunlight, but ester cleavage products are obtained in similar amounts. The unidentified materials appear to be similar to those formed in benzene solution.

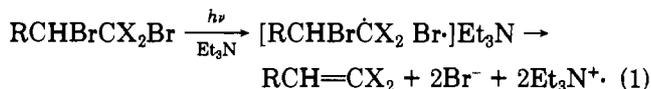
## DISCUSSION

The 3-(1',2'-dibromo-2',2'-dihaloethyl)-2,2-dimethylcyclopropanecarboxylates react photochemically to yield debromination, dehydrobromination, isomerization, and ester cleavage products (Figure 1). In the absence of hydrogen donors, i.e., in benzene or in the solid phase, polymerization and other radical reactions may be important degradation processes.

The reaction mechanism probably involves homolytic cleavage of a carbon–bromine bond from the most highly halogenated carbon (Sammes, 1973). The radical pair thus formed either can recombine or the residual alkyl fragment can collapse rapidly to yield an alkene and a second bromine atom (Figure 1). Formation of a bromocyclohexadiene and the isotope effect of reaction in chloroform vs. chloroform-*d* support the intermediacy of bromine radicals. Similar processes are reported for 1,2-dibromotetrachloroethane (Huyser and DeMott, 1963) and for *cis*-1,2-diiodobenzocyclobutene (Chapman et al., 1976). The reactive bromine radicals produced can either abstract

hydrogen from the solvent or radical scavenger or react with the ground-state substrate and its primary photoproducts, leading to the formation of polymeric material. Depletion of the bromine atom concentration leads to greater yields of debrominated material.

The reaction rate and debromination yields are increased on photolysis in the presence of triethylamine, which enhances electron transfer processes (eq 1) (Barltrop, 1973)



and the production of bromide ions from bromine radicals (Bunce et al., 1975). This effect is probably the combined result of depleting bromine radical concentration, thus minimizing secondary reactions, and of bromide-assisted ground-state concerted debromination (Baclocchi and Schiroli, 1969).

1'-Bromodeltamethrin and -cypermethrin may form by intramolecular abstraction of hydrogen from the 1' position by bromine while the radicals are still in the solvent cage or in the solid phase before they drift apart. Alternatively, these compounds may form by a concerted reaction eliminating hydrogen bromide. Both processes are reported in other systems (Sammes, 1973), but with tralomethrin the concerted process is not supported by the current study since the presence of an efficient hydrogen donor should not affect such a mechanism.

Isomerization of deltamethrin to the trans isomer involves the excited triplet state (Ruzo et al., 1976, 1977). The dimethylacrylate also forms from the triplet diradical by disproportionation to a carbene (Ruzo et al., 1977). The low yield of *trans*-tralomethrin and the absence of *trans*-tralocythrin in solution are puzzling since they form in substantial amounts in the solid phase. The presence of four bromine atoms in tralomethrin suggests that intersystem crossing in the excited state will be substantial and thus that the reaction may proceed from a triplet intermediate (Ruzo and Casida, 1980). Debromination can be sensitized efficiently with several energy donors but was not quenched by 1,3-cyclohexadiene, indicating that bond homolysis is probably a singlet process in the case of direct photolysis.

Ester cleavage products arise from both the substrate and its primary photoproducts. These compounds are

identical with those obtained from deltamethrin (Ruzo et al., 1977) and from the alcohol moiety of fenvalerate (Holmstead et al., 1978b).

The major primary processes in photodecomposition of tralomethrin and tralocythrin are debromination and other reactions centered on the acid moiety. Debromination may also contribute to the insecticidal activity of these pyrethroids (Ruzo et al., 1981). The reaction rate difference between the tetrabromo and dibromodichloro compounds is probably the result of lower bond energies in the former case. These tetrahaloethyl pyrethroids are efficiently degraded by low-energy UV irradiation and by sunlight, indicating that they are not likely to have prolonged environmental stability and persistence.

#### LITERATURE CITED

- Ackermann, P.; Bourgeois, F.; Drabek, J. *Pestic. Sci.* **1980**, *11*, 169.
- Baclocchi, E.; Schiroli, A. *J. Chem. Soc. B* **1969**, 554.
- Barltrop, J. A. *Pure Appl. Chem.* **1973**, *33*, 179.
- Bunce, N. J.; Safe, S.; Ruzo, L. O. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1607.
- Chapman, O. L.; Chang, C. C.; Rosenquist, N. R. *J. Am. Chem. Soc.* **1976**, *98*, 261.
- Elliott, M.; Janes, N. F. *Chem. Soc. Rev.* **1978**, *7*, 473.
- Holmstead, R. L.; Casida, J. E.; Ruzo, L. O.; Fullmer, D. G. *J. Agric. Food Chem.* **1978a**, *26*, 590.
- Holmstead, R. L.; Fullmer, D. G.; Ruzo, L. O. *J. Agric. Food Chem.* **1978b**, *26*, 954.
- Huyser, E. S.; DeMott, D. N. *Chem. Ind. (London)* **1963**, 1954.
- Roussel-Uclaf, French Demande 2364884, 1978.
- Ruzo, L. O.; Casida, J. E. *J. Chem. Soc., Perkin Trans. 1* **1980**, 728.
- Ruzo, L. O.; Gaughan, L. G.; Casida, J. E. *Pestic. Biochem. Physiol.* **1981**, in press.
- Ruzo, L. O.; Holmstead, R. L.; Casida, J. E. *Tetrahedron Lett.* **1976**, 3045.
- Ruzo, L. O.; Holmstead, R. L.; Casida, J. E. *J. Agric. Food Chem.* **1977**, *25*, 1385.
- Sammes, P. G. In "The Chemistry of the Carbon-Halogen Bond"; Patai, S., Ed.; Wiley: New York, 1973; Chapter 11, p 747.
- Yuan, T. S.; Wijnen, M. H. *J. Photochem.* **1980**, *12*, 109.

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