

Pyrethroid Photochemistry: Influence of the Chloro(trifluoromethyl)vinyl Substituent in Cyhalothrin

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The solution- and solid-phase photodecomposition of cyhalothrin (1) with a chloro(trifluoromethyl)vinyl substituent involves *E/Z* and *cis/trans* isomerization reactions and free-radical processes leading to decarboxylation, ester cleavage, proton abstraction, oxygen scavenging, and reactions with solvent-generated radicals. 1 yields a much greater proportion of decarboxylated materials than does its dichlorovinyl analogue cypermethrin (2). These decarboxylation products are also isomerized at the cyclopropyl and vinyl groups. Qualitatively similar results are obtained in hydrocarbon solvents, in aqueous acetonitrile, in anionic and cationic micelles, and on glass and soil surfaces. It is postulated that the enhanced decarboxylation is due to stabilization of the diradical intermediate by an increase in the *s* character of the lone electron orbital on C-1 of the cyclopropane resulting from electron withdrawal by the trifluoromethyl group through extended conjugation via the cyclopropyl ring. The non-cyano analogues of 1 and 2, halothrin (3) and permethrin (4), react at a slower rate, and decarboxylation is also found to be more important for 3 than for 4.

Many pyrethroids used in crop protection contain dihalovinyl substituents in the acid moiety (Elliott et al., 1978; Briggs et al., 1983). In (1*R*)-*cis*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylates, the potency is enhanced on replacement of the chlorine *cis* to the vinylic proton with a trifluoromethyl substituent, e.g. in cyhalothrin (1) (Bentley et al., 1980) (Figure 1) and biphenethrin (Plummer and Pincus, 1981).

The major photodegradation routes of the α -cyano-3-phenoxybenzyl and 3-phenoxybenzyl pyrethroids are well established (Ruzo, 1982, 1983a,b); e.g., deltamethrin (Ruzo et al., 1977), cypermethrin (2) (Figure 1) (Ruzo, 1983c; Takahashi et al., 1985), fenvalerate (Holmstead et al., 1978b; Mikami et al., 1980), and permethrin (4) (Holmstead et al., 1978a) undergo photoisomerization, ester cleavage, and free-radical processes; however, decarboxylation is prominent only with fenvalerate. The present interest in chloro(trifluoromethyl)vinyl-substituted pyrethroids prompted this study examining the photochemical behavior of 1 in organic, aqueous, and micellar solutions and as thin films on soils in comparison to the analogous dichlorovinyl compound 2.

MATERIALS AND METHODS

Spectroscopy and Analysis. Chromatographic and spectroscopic data for the principal compounds of interest are given in Tables I and II. Mass spectrometry (MS) was carried out with a Hewlett-Packard 5985B system operated in the electron impact (EI) or chemical ionization (CI, methane, 0.9 Torr) modes. All CI-MS analyses gave $[M + 29]^+$ and $[M + 41]^+$ signals with 10-15% and 2-5% relative intensities, respectively; only the quasi molecular ions $[MH]^+$ and important fragments and their relative intensities are tabulated. CI-MS was used for characterization and EI-MS for confirmation of molecular ion masses. Samples were introduced either by direct insertion (50-150 °C) or with previous gas chromatographic (GC) separation using a Hewlett-Packard 5840A instrument. A high-performance methylsilicone capillary column (10 m) was operated with temperature programming (20 °C/min) for photolysates of 1 (80-240 °C), 2 (160-240 °C), 3 (80-240 °C), and 4 (80-240 °C).

Nuclear magnetic resonance (NMR) spectroscopy was accomplished with a Bruker WM 300 instrument at 300 MHz (¹H) or 282 MHz (¹⁹F) for solutions in chloroform-*d* or solvents as specified. Chemical shifts are reported as ppm downfield from tetramethylsilane (¹H) or trifluoroethanol (CF₃CH₂OH, ¹⁹F). Coupling constants (*J*) are reported in hertz.

Electron-capture GC (EC-GC) with a Hewlett-Packard 5830A instrument involved a SP2100 (Supelco) glass column (0.6 m, 3 mm) operated at 220 °C (1 and 2) or 200 °C (3 and 4). The carrier gas (argon:methane = 19:1) flow was 30 mL/min.

Thin-layer chromatography (TLC) of photolysates was performed on 0.25-mm-thickness silica gel plates (60 F₂₅₄) developed twice with the following solvent systems: benzene-carbon tetrachloride (1:1), ether-hexane (1:5), or ethyl acetate-hexane (1:5), for separation of isomeric and decarboxylated products; acetone-hexane (1:5, 2:5), for other more polar products.

Pyrethroids and Standards. Relevant structures are shown in Figures 1-3. The *cis* and *trans* isomers of 1 and 3 were prepared from the corresponding isomers of acid 7 (1*RS*, X = CF₃) (a gift from FMC Corp., Princeton, NJ) by conversion to the acid chlorides with thionyl chloride and subsequent coupling with either α -cyano-3-phenoxybenzyl alcohol or 3-phenoxybenzyl alcohol, yielding 1 and 3, respectively, in >90% yield. Products were purified by TLC and characterized by CI-MS and NMR (Table I). *cis*- and *trans*-2 and -4 were generous gifts of Roussel-Uclaf (Paris, France).

Compounds 8-11 and 14-17 either were obtained commercially or were available from previous studies (Ruzo et al., 1977; Holmstead et al., 1978b; Ruzo, 1983c). Decarboxy pyrethroids (5, 6) were isolated by TLC, characterized by CI-MS and NMR (Table I), and used as standards for quantitation.

Photolysis Procedures. Ultraviolet irradiation was carried out at 300 nm with eight RPR3000 lamps in a Rayonette photoreactor (The Southern New England Ultraviolet Co., Middletown, CT). Solutions of *cis*- or *trans*-1-4 in Pyrex tubes were irradiated for 2-20 h in hexane, cyclohexane, or methanol (0.003 M) or in acetonitrile-water (1:4, 0.0002 M). Micellar solutions of 1 were examined as models for the formulated pesticide. They were prepared with sodium dodecyl sulfate (SDS; 0.5 M) and dodecyltrimethylammonium bromide (DTAB; 0.5 M) as anionic and cationic surfactants, respectively. *cis*-1 (1 mg) was added in acetonitrile (100 μ L) to the surfactant

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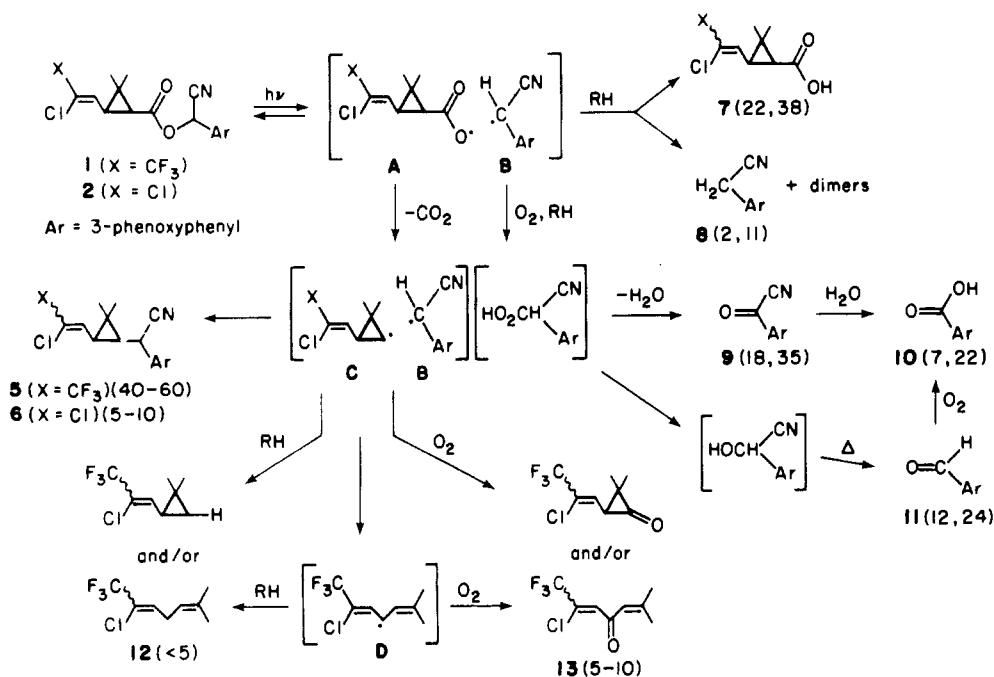


Figure 1. Photoproducts of cyhalothrin (1) and cypermethrin (2) and their designations and yields in hexane (shown in parentheses as they form from 1 and 2, respectively). Tentative alternative structures are given for 12 and 13.

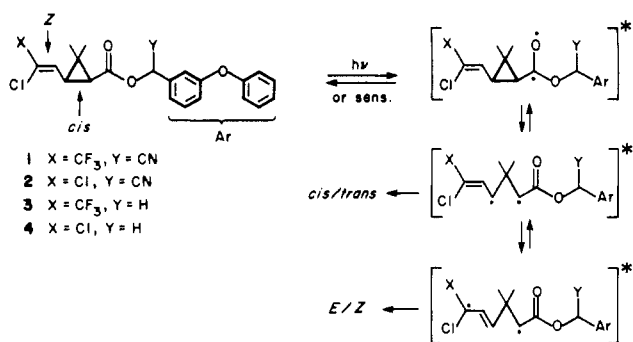


Figure 2. Triplet diradicals formed on direct or sensitized photolysis of chloro(trifluoromethyl)vinyl- and dichlorovinyl-substituted pyrethroids.

solution (2 mL), and the mixtures were sonicated (1–2 h). The samples were irradiated for 10–40 h and inspected directly (¹⁹F NMR) or after extraction (GC–MS). SDS solutions were worked up by addition of barium chloride (50 mg), extraction with hexane twice (2 mL), centrifugation, and drying the hexane over magnesium sulfate. DTAB solutions were treated in an identical manner, but precipitation was carried out with potassium iodide.

Photolysis of *cis*-1 on glass (25 μg/cm²) by sunlight (Berkeley, CA; June 1986) was carried out for 7 days, and

the photolysates were dissolved in acetonitrile (2 mL) and analyzed directly (¹⁹F NMR, GC–MS). Soil photolysis utilized Richvale, MSF, and Kracaws types whose characteristics have been reported previously (Gohre and Miller, 1986). The soils were dried and sieved through a screen (40 mm) to obtain uniform samples. *Cis*-1 (1 mg in hexane) was applied to thin soil layers (50 mg/cm²) to give a level of 50 μg of 1/cm² soil surface. These soil layers were exposed to sunlight (1–2 weeks) or ultraviolet light (48 h, 360 nm, RPR3500 lamps). The soils were extracted twice with methanol (5 mL) by sonication and centrifugation.

Characterization of Photoproducts. Photolysates from the various irradiation systems were routinely inspected by ¹⁹F NMR and GC–MS in the EI and CI modes. Some photolyses were carried out with the pyrethroid (0.01 M) in deuteriated solvents (cyclohexane-*d*₁₂, methanol-*d*₄) and the products examined by ¹H NMR. Photolysates were treated with diazomethane for GC–MS detection of acids (7, 10) as methyl esters. When available, standards were chromatographed (EC-GC or GC-MS) with photoproducts in mixtures or after TLC purification.

RESULTS

Identity and Distribution of Decarboxylation Products of 1–4 in Solutions (Table I; Figure 1). The

Other Acid Moiety Photoproducts			Other Alcohol Moiety Photoproducts		
Structure	Designation	Origin	Structure	Designation	Origin
	14	1 and 2 (hex, cyclohex)	Ar–H	17	1, hexane
	15	1 and 2 (hex, cyclohex)	ArCOOC ₆ H ₁₃	18	1, hexane
	16	1, all solvents	ArCOCH ₃	19	1, hexane + CH ₂ N ₂
	7-Me	1 and 2 methanol	ArCOC ₆ H ₁₁ (D ₁₁)	20	1, cyclohex (or C ₆ D ₁₂)
			ArCH=CHAr	21	1 and 2, cyclohex
				22	2, hexane
			ArCH(C ₆ H ₁₁ (D ₁₁))CN	23	2, cyclohex (or C ₆ D ₁₂)
				24	cyclohex (or C ₆ D ₁₂)

Figure 3. Other photoproducts of 1 and 2 in the indicated solvents.

Table I. Chromatographic and Spectroscopic Properties of Fluorinated Pyrethroids and Photoproducts Arising from Decarboxylation and Isomerization Processes

designation	R_t^a , min		NMR (δ)	CI-MS ^b
Fluorinated Pyrethroids				
1 (<i>Z</i> , <i>cis</i>) ^c	10.8		¹ H: 1.21 (CH ₃ , s), 1.28 (CH ₃ , s), 2.04 (CHCO, d, <i>J</i> = 9), 2.25 (CHCH:C, t, <i>J</i> = 9), 6.31 (CHCN, s), 6.82 (CHCH:C, dq, <i>J</i> = 9, 2), 7.0–7.4 (aromatics). ¹⁹ F: 8.35	450 ([MH] ⁺ , 42) 225 (1 Cl, 100) 208 (85)
1 (<i>Z</i> , <i>cis</i>) ^c	11.1		¹ H: 1.33 (CH ₃ , s), 1.35 (CH ₃ , s), 2.04 (CHCO, d, <i>J</i> = 9), 2.25 (CHCH:C, t, <i>J</i> = 9), 6.31 (CHCN, s), 6.82 (CHCH:C, dq, <i>J</i> = 9, 2), 7.0–7.4 (aromatics). ¹⁹ F: 8.35	450 ([MH] ⁺ , 28) 225 (1 Cl, 100) 208 (94)
1 (<i>Z</i> , <i>trans</i> , α RS)	10.9		¹ H: 1.23 (CH ₃ , s), 1.26 (CH ₃ , s), 1.27 (CH ₃ , s), 1.38 (CH ₃ , s), 1.82 (CHCO, d, <i>J</i> = 5), 1.84 (CHCO, d, <i>J</i> = 5), 2.46 (2 CHCH:C, m), 6.12 (CHCH:C, dq, <i>J</i> = 5, 2), 6.15 (CHCH:C, dq, <i>J</i> = 5, 2), 6.37 (CHCN, s), 6.39 (CHCN, s), 7.0–7.4 (aromatics). ¹⁹ F: 8.16	450 ([MH] ⁺ , 26) 225 (1 Cl, 100) 208 (22)
3 (<i>E</i> , <i>Z</i> , <i>cis</i>)	10.3	<i>Z</i>	¹ H: 1.27 (CH ₃ , s), 1.28 (CH ₃ , s), 2.02 (CHCO, d, <i>J</i> = 9.1), 2.17 (CHCH:C, t, <i>J</i> = 9.1), 5.08 (CH ₂ O, s), 6.92 (CHCH:C, dd, <i>J</i> = 9, 0.2), 7.0–7.4 (aromatics). ¹⁹ F: 8.47	425 ([MH] ⁺ , 17) 405 ([M - F] ⁺ , 1 Cl, 26) 223 (32), 183
		<i>E</i>	¹ H: 1.23 (CH ₃ , s), 1.25 (CH ₃ , s), 1.94 (CHCO, d, <i>J</i> = 9.1), 2.17 (CHCH:C, t, <i>J</i> = 9.1), 5.07 (CH ₂ , s), 6.63 (CHCH:C, d, <i>J</i> = 9.1), 7.0–7.4 (aromatics). ¹⁹ F: 8.47	
3 (<i>E</i> , <i>Z</i> <i>trans</i>)	9.8	<i>Z</i>	¹ H: 1.22 (CH ₃ , s), 1.29 (CH ₃ , s), 1.81 (CHCO, d, <i>J</i> = 9), 2.42 (CHCH:C, t, <i>J</i> = 9), 5.08 (CH ₂ O, s), 6.19 (CHCH:C, dq, <i>J</i> = 9, 2), 7.0–7.4 (aromatics). ¹⁹ F: 8.27	425 ([MH] ⁺ , 22) 405 ([M - F] ⁺ , 1 Cl, 38) 223 (41), 183
		<i>E</i>	¹ H: 1.19 (CH ₃ , s), 1.25 (CH ₃ , s), 1.73 (CHCO, d, <i>J</i> = 7), 2.41 (CHCH:C, t, <i>J</i> = 7), 5.08 (CH ₂ O, s), 5.87 (CHCH:C, d, <i>J</i> = 7), 7.0–7.4 (aromatics). ¹⁹ F: 8.27	
Decarboxylated Photoproducts				
decarboxy 3	8.5, 8.7	<i>Z</i> , <i>cis</i>	¹ H: 5.96 (CHCH:C, d, <i>J</i> = 9.6). ¹⁹ F: 8.80	381 ([MH] ⁺ , 38)
		<i>Z</i> , <i>trans</i>	¹ H: 5.84 (CHCH:C, d, <i>J</i> = 9.6). ¹⁹ F: 8.74	361 ([M - F] ⁺ , 1 Cl, 62)
		<i>E</i> , <i>cis</i>	¹ H: 6.23 (CHCH:C, dq, <i>J</i> = 9.6, 2.5). ¹⁹ F: 15.04 (d, <i>J</i> = 2.5)	211 (40), 183 (100)
		<i>E</i> , <i>trans</i>	¹ H: 6.11 (CHCH:C, dq, <i>J</i> = 9.6, 2.2). ¹⁹ F: 15.29 (d, <i>J</i> = 2.2)	
5 (<i>E</i> , <i>Z</i> , <i>trans</i> α RS)	9.7, 10.3	<i>E</i>	¹ H: 6.02 and 6.13 (CHCH:C, dq, <i>J</i> = 10, 2). ¹⁹ F: 15.03 and 14.97 (d, <i>J</i> = 2)	406 ([MH] ⁺ , 1 Cl, 86) 386 ([M - F] ⁺ , 1 Cl, 41) 379 ([M - CN] ⁺ , 100)
		<i>Z</i>	¹ H: 5.70 and 5.87 (CHCH:C, d, <i>J</i> = 10). ¹⁹ F: 8.41 and 8.40	406 ([MH] ⁺ , 1 Cl, 92) 386 ([M - F] ⁺ , 1 Cl, 32)
5 (<i>E</i> , <i>Z</i> , <i>cis</i> , α RS)	9.9, 10.7	<i>E</i>	¹ H: 6.18 and 6.25 (CHCH:C, dq, <i>J</i> = 8.5, 2). ¹⁹ F: 14.6 (2 overlapping d)	379 ([M - CN] ⁺ , 100) 372 ([MH] ⁺ , 26)
		<i>Z</i>	¹ H: 5.98 and 6.39 (CHCH:C, d, <i>J</i> = 8.5). ¹⁹ F: 8.53 and 8.44	345 ([M - CN], 2 Cl, 100) 210 (32)
6 (<i>cis</i> , <i>trans</i>)	6.5, 7.2		¹ H: 3.28 (CHCN, d, <i>J</i> = 11.2), 3.41 (CHCN, d, <i>J</i> = 11.2), 5.38 (CHCH:C, d, <i>J</i> = 10.9), 5.50 (CHCH:C, d, <i>J</i> = 10.9)	

^a Products analyzed at 80–240 °C (20 °C/min) by GC-MS. ^b All [MH]⁺ confirmed in EI-MS. ^c Diastereomeric pairs of enantiomers (1*R*, α S + 1*S*, α R) and (1*R*, α R + 1*S*, α S).

Table II. Chromatographic and Spectroscopic Properties of Photoproducts Arising from Ester Cleavage and Other Processes

acid moiety			alcohol moiety			others		
design- nation	R_t^a , min	CI-MS ^b	design- nation	R_t^a , min	CI-MS ^b	design- nation	R_t^a , min	CI-MS ^b
7-Me (X = Cl)	2.6	223 ([MH] ⁺ , 2 Cl, 100), 163 (62)	8	7.2	210 ([MH] ⁺ , 100)	14	5.6	308 ([MH] ⁺ , 100)
			9	6.9	227 ([MH] ⁺ , 52), 197 (100)	22	4.5	290 ([MH] ⁺ , 2 Cl, 100)
7 (X = CF ₃)	3.7	243 ([MH] ⁺ , 1 Cl, 100), 223 (62)	10-Me	6.3	229 ([MH] ⁺ , 100)	24	1.6	99 ([MH] ⁺ , 100)
			11	6.4	199 ([MH] ⁺ , 100)			
12	1.9	199 ([MH] ⁺ , 1 Cl, 28), 179 (1 Cl, 100)	17	4.5	171 ([MH] ⁺ , 100)			
			18	8.3	299 ([MH] ⁺ , 100)			
			19	6.2	213 ([MH] ⁺ , 100)			
13	3.0, 3.1 3.2, 3.3	213 ([MH] ⁺ , 1 Cl, 100)	20	11.0	281 ([MH] ⁺ , 100)			
			21	7.9	365 ([MH] ⁺ , 100)			
			23	7.1	303 ([MH] ⁺ , 100), 276 (92)			

^a Products arising from 1 analyzed at 80–240 °C (20 °C/min) and from 2 at 160–240 °C (20 °C/min) by GC-MS. ^b All [MH]⁺ confirmed by EI-MS.

major difference in the photolyses of 1 and 2 is in the yield of decarboxylated products, e.g. 40% yield of 5 from *trans*-1 while 6 is only found in 8% yield from *trans*-2 after 3-h irradiation in cyclohexane. Longer irradiation times of *trans*-1 and *trans*-2 under these conditions result in continued accumulation of 5 but not of 6 and in the formation of a great variety of other products considered later.

Although photoisomerization to the *trans* isomer predominates in the photolysis of *cis*-2, sufficient decarboxylation to 6 is obtained for isolation and characterization (¹H NMR, GC-MS). Decarboxylation is readily apparent

for *cis*-3 but not for *cis*-4 on irradiation in cyclohexane.

Decarboxylation products (5) isolated by TLC from photolysates of both *cis*-1 and *trans*-1 yield eight clearly resolved doublet (³J_{HH}) signals (vinyl protons) in ¹H NMR corresponding to the *E/Z*, *cis/trans*, and α RS enantiomer pairs. Of these eight doublets, four are further split into poorly resolved quartets (⁴J_{HF}) corresponding to the *E* isomers. ¹⁹F NMR also shows eight signals: four of them as doublets (⁴J_{HF}) and the other four as singlets. On the basis of the magnitude of the ⁴J_{HF} values and the ¹⁹F chemical shifts, the isomer composition in the decarbox-

ylated fraction is similar to that in the intact ester fraction, i.e., $Z,trans > E,trans > Z,cis > E,cis$. *cis*-3 decarboxylates, yielding four isomers evident as two peaks in GC-MS or EC-GC, four 1H NMR doublets ($^3J_{HH}$) corresponding to the vinyl protons (two of them further split into poorly resolved quartets due to $^4J_{HF}$), and two doublets ($^4J_{HF}$) and two singlets in ^{19}F NMR.

Identity and Distribution of Photoisomerization Products of 1-4 in Solutions (Table I; Figure 2). Pyrethroids 1-4 undergo isomerization as the most efficient reaction, forming *cis/trans* mixtures from 2 and 4 and *E/Z*, *cis/trans* isomerization products from 1 and 3. The *Z,trans* esters are always found in greater yield, approximately in a 3:2 ratio with the *Z,cis* isomers. *Cis* isomers exhibit greater J values for coupling between the C-1 and C-3 cyclopropyl protons, and *E* and *Z* esters can be distinguished by the magnitude of the four-bond coupling of the vinyl proton with fluorine. Although isomeric mixtures arising from 1 and 2 could not be fully separated by GC or TLC, 1H NMR clearly resolves the vinyl proton signal as illustrated with 3. A singlet ^{19}F NMR signal is obtained for each of *Z,cis*- and *Z,trans*-3. The 1H NMR of isomeric 1 is more difficult to analyze since it includes (*1RS*), *E/Z,cis/trans* and αRS components (a total of 16 isomers) with considerable overlap of signals in the regions of interest. Although the isomerization process is only partially established from the present results, it is supported by previous findings with other cyanophenoxybenzyl esters (Ruzo et al., 1977; Takahashi et al., 1985) and by the isomeric composition of the decarboxylated products obtained, as discussed previously. Pyrethroid 2 also isomerizes readily to mixtures rich in *trans* materials (Takahashi et al., 1985; this study).

Comparative Photolysis Rates of 1-4 in Solutions. Reactivities are compared on the basis of the recovered *cis/trans* isomer mixtures following irradiation at 300 nm. The *trans* isomers of 1 and 2 irradiated in cyclohexane or cyclohexane- d_{12} are 52% and 34% reacted (3 h), respectively, without a significant solvent isotope effect. The greater reactivity of 1 than of 2 is also evident in hexane, methanol, and acetonitrile-water (1:4). The product distributions are similar in all the solvents studied, with minor variations due to reaction with the solvent (Figure 3). 3 and 4 are photolyzed nearly 5-fold slower than their α -cyano analogues (1, 2).

Identity and Distribution of Photocleavage Products of 1 and 2 in Solutions (Table II; Figures 1 and 3). In methanol- d_4 the corresponding esters of 7 and 10 are obtained, while 5 exhibits detectable amounts of deuterium, probably incorporated at the benzylic methine from exchange reactions (Ruzo et al., 1977). Compounds 8 and 12 are found to incorporate deuterium when photolyzed in cyclohexane- d_{12} ; 20 and 23 contain the cyclohexyl- d_{11} moiety. Compounds 12 and 13 are not characterized beyond their molecular weights, but both types of products are probably formed in each case because at least four GC-MS peaks are observed for 13 with the same mass and similar retention time (R_t). Concentrated (0.01 M) solutions generally contained greater amounts of 18 and 20-23. Additionally, in cyclohexane solutions substantial amounts of cyclohexanone (24) are detected (GC-MS). Yields of 12-23 were generally low (<5%) in all systems.

Photolysis of 1 in Heterogeneous Media. Irradiation of *Z,cis*-1 in aqueous acetonitrile was carried out to ~20% conversion. In addition to isomerization of the vinyl and cyclopropyl groups, the only other products detected arise from decarboxylation (70-80%) and to a lesser degree from ester cleavage yielding acid 7 ($X = CF_3$) (<5%) and di-

meric products. In contrast, *cis*-2 irradiated in parallel (5 h) reacts at a comparable rate but yields 6 only as a minor product, 7 ($X = Cl$) being the major photoproduct. [For more complete studies on the behavior of 2 in aqueous systems, see Ruzo (1983c) and Takahashi et al. (1985).]

Anionic (SDS) and cationic (DTAB) micellar solutions of *Z,cis*-1 were also examined (^{19}F NMR, GC-MS) after photolysis. Reaction in SDS solutions is ~1.5-fold slower than in hexane or DTAB, although rates could not be accurately reproduced with DTAB due to variable coating of the Pyrex surface with undissolved pyrethroid. The major products are the isomers of 1 and 5; minor amounts of acids 7 ($X = CF_3$) and 10 are also formed.

Although not quantitated, exposure of *Z,cis*-1 to sunlight on glass surfaces as a thin film results in isomerization and decarboxylation (^{19}F NMR, GC-MS). Aldehyde 11 and acids 7 ($X = CF_3$) and 10 are also detected. The same products are obtained when *Z,cis*-1 absorbed on several soil types is exposed to sunlight or 360-nm ultraviolet light. Loss of 1 on soils proceeded 4-fold slower than on glass, presumably due to quenching or light shielding effects.

Benzophenone-sensitized photolysis (360 nm) of 1-4 in cyclohexane leads only to isomeric products identical with those obtained on direct irradiation, and in the case of 1 and 2 trace amounts of 14 are also detected.

Irradiation of 1 in oxygen-saturated cyclohexane (300 nm) yields decreased amounts of 5 and enhanced formation of 9-11, 13, 15, and 16. Photolyzed 2 in oxygenated solution exhibits a similar product distribution (Figures 1 and 3) with greater yields of 22 than in nitrogen-saturated cyclohexane.

DISCUSSION

Figure 1 gives the proposed photolysis reactions of 1 and 2 other than the isomerizations shown in Figure 2. The electron-withdrawing properties of the trifluoromethyl group have a marked effect on the decarboxylation reactions but little influence on other processes.

Pyrethroids containing the cyclopropyl group generally undergo decarboxylation only as a minor process (Ruzo, 1983a) relative to fenvalerate (Holmstead et al., 1978b; Mikami et al., 1980). We now find that 1 is extensively decarboxylated relative to 2. This extrusion of carbon dioxide appears to take place after isomerization, the most efficient photoprocess (Miyamoto and Mikami, 1983), and only involves the radical pair C-B and not the rearranged radical D (Figure 1), based on NMR evidence. The radical nature of the intermediates has been conclusively established with fenvalerate by ESR with trapping experiments (Mikami et al., 1985). It is interesting that 2 is found to decarboxylate as a minor process in some cases (Ruzo, 1983c; this study) and not in others (Takahashi et al., 1985). However, in no case does this reaction result in >15% yield of decarboxylated material. A possible explanation for increased decarboxylation in the presence of a vinyl trifluoromethyl substituent may involve increased s character of the lone electron orbital on C-1 of the cyclopropane (due to electron withdrawal by trifluoromethyl) through extended conjugation via the cyclopropyl ring, thus stabilizing C. Decarboxylation of 1 is observed in every system studied, including homogeneous and heterogeneous solutions and thin films on glass and soil.

Isomerization is a common process for pyrethroids containing the cyclopropyl group (Ueda and Matsui, 1971; Ruzo, 1983a) proceeding via a triplet excited state (Ruzo and Casida, 1980). A previously reported case involving a formylmethylvinyl derivative of phenothrin (Ruzo et al., 1982), a chrysanthemate-derived pyrethroid metabolite,

and photoproduct indicates that *E/Z* as well as *cis/trans* interconversions are possible from the triplet intermediate. The present study supports the postulated extended π conjugation across the cyclopropyl ring from the carboxylate to the vinyl substituent. Thus, **1** and **3** exhibit both *cis/trans* and *E/Z* isomerization. The preferred products are obtained in amounts consistent with the thermodynamic parameters of the excited-state geometry.

A great variety of additional photoproducts is observed with **1** and **2** (Figure 3). Most of these arise from radical processes, as supported by deuterium incorporation, dimerization reactions, and oxygen scavenging. Similar species are identified from previous studies on **2** (Ruzo, 1983c; Takahashi et al., 1985), deltamethrin (Ruzo et al., 1977), and fenvalerate (Holmstead et al., 1978b; Mikami et al., 1980).

Oxidation reactions in the vinyl substituent lead to **15**, **16**, and probably **22**. A recent study on **2** (Takasashi et al., 1985) detected the anhydride of *cis*-caronic acid derived from **15**. These products may arise from reaction with ozone formed during photolysis since caronaldehydes are detected from a variety of pyrethroids (Ruzo et al., 1982, 1986) and trifluoroacetyl chloride is obtained for **3** on direct reaction with ozone (Ruzo et al., 1986). This reaction may be the basis for the formation of **22** from **2**, i.e. by addition of phosgene (from ozonolysis) to the cyanophenoxybenzyl radical or anion with subsequent elimination of water. Other oxidation products in the alcohol moiety (**9**–**11**, **18**–**20**) probably arise from radical **B** via various oxygen-scavenging processes.

The chloro(trifluoromethyl)vinyl substituent examined here in **1** and **3** is present in a variety of other insecticidally potent pyrethroids. These compounds may also undergo enhanced photodecarboxylation relative to the dichlorovinyl analogues.

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Registry No. **1**, 68085-85-8; **1** (*Z,cis, 1R, α S*), 76703-62-3; **1** (*Z,cis, 1S, α R*), 76703-65-6; **1** (*Z,cis, 1R, α R*), 76703-63-4; **1** (*Z,cis, 1S, α S*), 76703-64-5; **2**, 52315-07-8; **3**, 71698-60-7; **3** (*Z,cis*), 110508-49-1; **3** (*E,cis*), 74111-97-0; **3** (*Z,trans*), 107794-42-3; **3** (*E,trans*), 74111-96-9; **3** (decarboxy, *Z,cis*), 110457-98-2; **3** (decarboxy, *Z,trans*), 110508-50-4; **3** (decarboxy, *E,cis*), 110508-51-5;

3 (decarboxy, *E,trans*), 110508-52-6; **4**, 52645-53-1; **5**, 110457-91-5; **6**, 110457-92-6; **7**, 74609-46-4; **7-Me**, 61898-95-1; **8**, 51632-29-2; **9**, 61775-25-5; **10**, 3739-38-6; **11**, 39515-51-0; **12**, 110457-93-7; **13**, 110457-94-8; **14**, 110457-95-9; **15**, 25312-79-2; **16**, 76-05-1; **17**, 101-84-8; **18**, 69200-14-2; **19**, 32852-92-9; **20**, 110472-08-7; **21**, 110457-96-0; **22**, 110457-97-1; **23**, 110472-09-8; **24**, 108-94-1.

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