Pyrethroid Photochemistry: Photooxidation Reactions of the Chrysanthemates Phenothrin and Tetramethrin

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The major identified photoproducts of *trans*-phenothrin, irradiated in the solid phase by sunlight and in oxygenated benzene solution at 360 nm, are formed by oxidation of the isobutenyl substituent as follows: the epoxide; the alcohol, aldehyde, and carboxylic acid derivatives from oxidation at the (*E*)-methyl group; the caronaldehyde and caronic acid derivatives from cleavage upon ozonolysis; the hydroperoxide from ene reaction at the 1′ position. Minor products result from further reactions of the hydroperoxide and from trans/cis interconversion and ester cleavage. Trans/cis isomerization is the only observed photoprocess in deoxygenated benzene solution at 360 nm. *trans*-Tetramethrin reacts by similar pathways but also undergoes oxidation at the allylic position in the alcohol moiety. The variety of oxidation products observed arises from the different types of attack, depending on whether singlet oxygen, triplet oxygen, or ozone is involved.

Environmental degradation of chrysanthemates involves extensive oxidation at their isobutenyl substituent (Casida and Ruzo, 1980; Ruzo, 1981). Stepwise photooxidation of the (*E*)-methyl group yields the alcohol derivative of allethrin (Ruzo et al., 1980) and the respective alcohol, aldehyde, and carboxylic acid derivatives of allethrin, pyrethrin I, dimethrin, and tetramethrin possibly with modified alcohol moieties (Chen and Casida, 1969). Caronaldehyde and caronic acid esters are also formed on photolysis of allethrin, pyrethrin I, dimethrin, tetramethrin (Chen and Casida, 1969), and phenothrin (Nambu et al., 1980); the ozonide intermediate is reported in the case of phenothrin (Nambu et al., 1980). Epoxidation is a major photoreaction of allethrin and resmethrin (Ueda et al., 1974; Ruzo et al., 1980). Only a portion of the photoproducts are characterized, in part because extensive oxidation occurs in both the acid and alcohol moieties. The 3-phenoxybenzyl group of phenothrin confers greater overall photostability than the alcohol moieties of earlier pyrethroids (Chen and Casida, 1969; Elliott et al., 1973; Ruzo and Casida, 1980).

The present report considers the light-mediated oxidation reactions of the relatively unstable *trans*-tetramethrin and the more stable *trans*-phenothrin with singlet and triplet oxygen and with ozone.

MATERIALS AND METHODS

Chromatography, Spectroscopy, and Analyses. Thin-layer chromatography (TLC) employed silica gel F-254 chromatoplates with 0.25-mm gel thickness for analyses and 0.5 mm for preparative isolations with solvent systems and R_f values given in Table I. Unlabeled products were visualized by their quenching of gel fluorescence at 254 nm and radioactive products by radioautography. The photoproducts were extracted from the silica gel by sonication in ether (recovery was >80%).

Gas–liquid chromatography (GLC) utilized two systems (Table I): A, an SP-2100 open tubular column in a Hewlett-Packard 5830A instrument equipped with a ^{63}Ni electron capture detector and on on-line computer to calculate retention times (R_t) and normalized areas; B, an OV-25-packed column in a Varian Aerograph 1400 instrument with a flame ionization detector. Quantitation involved authentic standards or assumed similar electron capture or flame ionization responses to those of available standards of appropriate structure and R_f.

Chemical ionization mass spectra (CI-MS) were recorded with a Finnigan 3200 instrument equipped with a System Industries 150 data system. Methane (0.7–0.9 torr) was the reagent gas. The ionization voltage was 40–70 eV, and inlet probe temperatures were 40–200 °C as appropriate. Masses and percent intensities are given for quasi-molecular ions (M + 1) and other important fragments (Table II).

GLC–MS utilized a Finnigan 9500 gas chromatograph interfaced with the MS system as above. A glass column (2 m; 0.4-cm i.d.) packed with 5% OV-101 on Chromosorb GHP was operated isothermally (220 °C, for cochromatography and quantitation) or with temperature programming (120–240 °C, for survey experiments). The methane carrier gas flow was 15–20 mL/min.

Nuclear magnetic resonance (NMR) spectra were obtained with a 90- or 250-MHz spectrometer equipped with a Fourier transform computer. Samples were dissolved in deuteriochloroform containing 0.2% tetramethylsilane (Me_4Si), chemical shifts (δ) are reported as ppm downfield from Me_4Si, and coupling constants (J) are given in hertz (Table III)

Pyrethroids and Their Derivatives. Structures of compounds utilized in this study are shown in Figure 1, and relevant CI–MS and NMR spectral features are given in Tables II and III, respectively.

(1*R*,*trans*)-Phenothrin (**1a**) and (1*R*,*cis*)-phenothrin (*c*-**1a**) were obtained from Roussel-Uclaf (Paris, France) and (1*RS*,*trans*)-tetramethrin (**1b**) and (1*RS*,*cis*)-tetramethrin (*c*-**1b**) were obtained from Sumitomo Chemical Co. (Osaka, Japan). The specific activity of (1*R*,*trans*)-[*carboxyl*-^{14}C]tetramethrin was 2.2 mCi/mmol (Yamamoto and Casida, 1968).

Epoxides (*RS*)-**2a** and (*RS*)-**2b** were obtained as diastereomeric mixtures (1′*RS*) in >90% yield on treatment of **1a** and **1b** with excess *m*-chloroperbenzoic acid (MCPBA) in dichloromethane. The solution was washed with saturated NaCl, and the products were purified by TLC (CE). The epoxides gave a blue-violet color with 4-(*p*-nitrobenzyl)pyridine (Hammock et al., 1974).

Alcohol **3a** was prepared by reduction of aldehyde **4a** with excess $NaBH_4$ in ether. After the mixture was stirred overnight and extracted with water, the ether-soluble products were chromatographed (CE) to obtain the alcohol in 80% yield. Acetate **3a**-OAc was prepared by reacting the alcohol with acetyl chloride in benzene containing equivalent pyridine. In the synthesis of **3b**, the aldehyde

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Table I. Gas-Liquid and Thin-Layer Chromatographic Properties of *trans*-Phenothrin (1a), *trans*-Tetramethrin (1b), and Their Derivatives

product	1a and deriv., GLC R_t, min, in system A[a,b]	1a and deriv., TLC R_f[c]				1b and deriv., TLC R_f[c]			
		CA	CE	DE	HE	CA	CE	DE	HT
1	6.2		0.85	0.81	0.60	0.69	0.51	0.58	0.70
c-1	6.0		0.86	0.85	0.62		0.55	0.67	
(*RS*)-2	7.3	0.68	0.65, 0.58[d]	0.60, 0.52	0.37, 0.30	0.58	0.34	0.33	0.59, 0.54
3	(17.1)[e]	0.31	0.20	0.21	(0.31)	0.27	0.05	0.11	0.29
4	12.1	0.67	0.53	0.56	0.23	0.56	0.23	0.35	0.51
c-4	12.0		0.68		0.30				
5	(13.8)	0.12	(0.64)	(0.62)	(0.31)	(0.60)	(0.26)	(0.38)	(0.54)
6	dec	0.70	0.58	0.64	0.28	0.54	0.28	0.44	0.48
7	(6.4)	0.12	(0.74)		(0.42)				
(*RS*)-8	dec	0.56/0.59	0.45	0.38	0.23	0.57	0.22	0.36	0.52
(*RS*)-9	(13.4)	(0.75)	0.26	0.25	(0.40)				
11	(0.9)		0.46	0.50	0.35				
12	(1.5)	(0.71)	0.25	0.31	0.15	0.20	0.06	0.10	0.31
13	1.9	0.70	0.74		0.47				
14	3.1	(0.70)	(0.70)	(0.72)	(0.51)				

[a] System A utilizes a glass open tubular column (12 m; 0.25-mm i.d.) coated with SP-2100 with operating temperatures of 300 °C (injector and detector) and 220 °C (oven, isothermal). Helium was the carrier gas (split ratio, 1:30), and argon-methane (19:1) was the makeup gas for the detector. The R_t for 10a is 8.0 min. [b] System B for GLC utilizes a glass packed column with 5% OV-25 on Chromosorb W (1.2 m; 0.4-cm i.d.) with operating temperatures of 250 °C (injector and detector) and 190 or 210 °C (oven isothermal). Nitrogen was the carrier gas at 20 mL/min. R_t values (minutes) are as follows: 190 °C, *Z*-*c*-4a, 12.9, *Z*-4a, 14.9, *E*-*c*-4a, 14.9, and *E*-4a, 17.2; at 210 °C, 1a, 1.8, (*RS*)-2a, 3.0, 5a-Me, 7.5, and 7a-Me, 2.2. [c] Silica gel 60 F-254 chromatoplates (precoated; 0.25-mm thickness; 20 × 20 cm) with solvent systems as follows: CA, chloroform–acetone (9:1); CE, carbon tetrachloride–ether (3:1); DE, dichloromethane–ether (19:1); HE, hexane–ether (2:1); HT, hexane–toluene–ethyl acetate–methanol (9:6:4:1). TLC system CE separates (*E*)-4a and (*E*)-*c*-4a as indicated but the corresponding *Z* isomers are not separated from the *E* isomers. 15b and 16b give R_f values of 0.24 and 0.17, respectively, in CA and 0.34 and 0.24, respectively, in HT. [d] Two R_f values indicate separation of diastereomeric pairs. [e] Parentheses designate methyl esters or acetyl derivatives as appropriate.

Table II. Chemical Ionization (Methane)–Mass Spectral Data for *trans*-Phenothrin (1a), *trans*-Tetramethrin (1b), and Their Derivatives

compound[a]	*m/e* (rel intensity)			
	$(M + 1)^+$	base peak	acylium ion	other ions
	Phenothrin (1a) and Derivatives			
1a	351 (2.5)	183	151 (32)	365 (M + 15), 333 (2), 305 (2)
(*RS*)-2a	367 (1.5)	183	167 (39)	349 (3), 139 (51)
3a	367 (0.8)	183	167 (23)	349 (18)
3a-OAc	409 (0.5)	183		365 (6), 349 (9)
4a	365 (4)	183	165 (9)	
c-4a	365 (11)	183	165 (7)	393 (M + 29, 2), 137 (6)
5a-Me	395 (3)	183	195 (38)	363 (14)
6a	325 (4)	183		307 (7), 199 (82)
7a-Me	355 (6)	183	155 (6)	383 (M + 29, 1), 323 (13)
(*RS*)-8a	382 (0.5)[b]	183	167 (17), 165 (17)	365 (3), 349 (5)
(*RS*)-9a	367 (0.2)	183	167 (11)	349 (6)
(*RS*)-9a-OAc	409 (1)	183	167 (21)	365 (1), 349 (6)
	Tetramethrin (1b) and Derivatives			
1b	332 (5.5)	164	151 (13.5)	314 (9.5), 286 (20)
(*RS*)-2b	348 (0.5)	123	167 (17)	330 (2), 164 (82)
3b	348 (0.5)	164	167 (15)	330 (4)
4b	346 (3)	164	165 (25)	327 (2), 181 (13)
5b-Me	376 (0.5)	164	195 (19)	344 (3), 181 (21)
6b	306 (2)	164		334 (M + 29, 5), 288 (14)
(*RS*)-8b	364 (0.5)	164	165 (11)	346 (3), 181 (5)
	3-Hydroxy-3,4,5,6-tetrahydrophthalimide Derivatives			
15b		180	151 (34)	330 (M - 17, 0.5), 123 (30)
16b		180	167 (20)	123 (62)

[a] See Figure 1. Me = methyl ester. OAc = acetoxy derivative. [b] Molecular ion (M^+).

derivative of methyl *trans*-chrysanthemate (4, R = H; 0.3 mmol; from SeO_2 oxidation of 1, R = H) was reduced with excess $NaBH_4$ in methanol containing 0.5% $NaHCO_3$ at 25 °C to obtain the hydroxy ester (90%) [NMR δ 4.05 (s, CH_2OH)]. Base hydrolysis (5% KOH in 1:1 methanol–water at 25 °C) gave the hydroxy acid (0.27 mmol) which was then reacted with *N*-(chloromethyl)-3,4,5,6-tetrahydrophthalimide (0.32 mmol) (Miyamoto and Suzuki, 1973) in tetrahydrofuran (THF) containing equivalent triethylamine. After the mixture was refluxed overnight, the THF was removed, and the residue was redissolved in ether and successively extracted with dilute HCl and saturated $NaHCO_3$. Purification by TLC (CA) gave **3b** in 35% yield.

Table III. ^{1}H Nuclear Magnetic Resonance Spectral Data for *trans*-Phenothrin (1a), *trans*-Tetramethrin (1b), and Their Derivatives

compound[a]	NMR chemical shifts, δ, for acid moiety[b]		
	C-1′	C-4′/C-3′	C-2 ring methyls
1a, 1b	4.85 (d, J = 7,[d] 1 H)	1.69 (s, 6 H)	1.11, 1.26 (s, 3 H)
(*RS*)-2a, (*RS*)-2b	2.50 (d, J = 8, 1 H), 2.70 (d, J = 4, 1 H)	1.23, 1.27, 1.31, 1.34 (24 H)	
3a, 3b	5.22 (d, J = 9, 1 H)	1.80 (s, 3 H), 4.05 (d, J = (d, J = 2.5, 2 H)	1.26, 1.30 (s, 3 H)
4a, 4b	6.15 (d, J = 10, 1 H)	1.85 (s, 3 H), 9.36 (s, 1 H)	1.27, 1.32 (s, 3 H)
c-4a	6.92 (d, J = 9, 1 H)	1.83 (s, 3 H), 9.41 (s, 1 H)	1.29, 1.34 (s, 3 H)
5a-Me, 5b-Me[c]	7.02 (d, J = 9, 1 H)	1.90 (s, 3 H)	1.24, 1.31 (s, 3 H)
6a	9.57 (s, 1 H)		1.29, 1.32 (s, 3 H)
7a-Me			1.24, 1.28 (s, 3 H)
(*RS*)-8a	3.99 (d, J = 11, 1 H), 3.97 (d, J = 11, 1 H)	1.75 (s, 3 H), 1.84 (s, 3 H), 4.95-5.07 (m, 4 H)	1.15-1.30 (m, 12 H)
(*RS*)-9a	3.75 (d, J = 12, 1 H), 3.77 (d, J = 12, 1 H)	1.71 (s, 3 H), 1.92 (s, 3 H), 4.71-5.00 (m, 4 H)	1.20-1.60 (m, 12 H)

[a] See Figure 1. [b] Spectra measured in deuteriochloroform with Me_4Si as the internal standard. The cyclopropane ring protons are generally obscured and are unassigned. Resonances due to the alcohol moiety are as follows: phenothrin, δ 5.10 (m, 2 H, $ArCH_2O$), 6.90-7.50 (m, 9 H, aromatics); tetramethrin, δ 1.78 (m, 4 H, 2 :CCH_2CH_2), 2.38 (m, 4 H, 2 :CCH_2), 5.51 (m, 2 H, NCH_2O). [c] Methoxy resonance at δ 3.7. [d] In hertz.

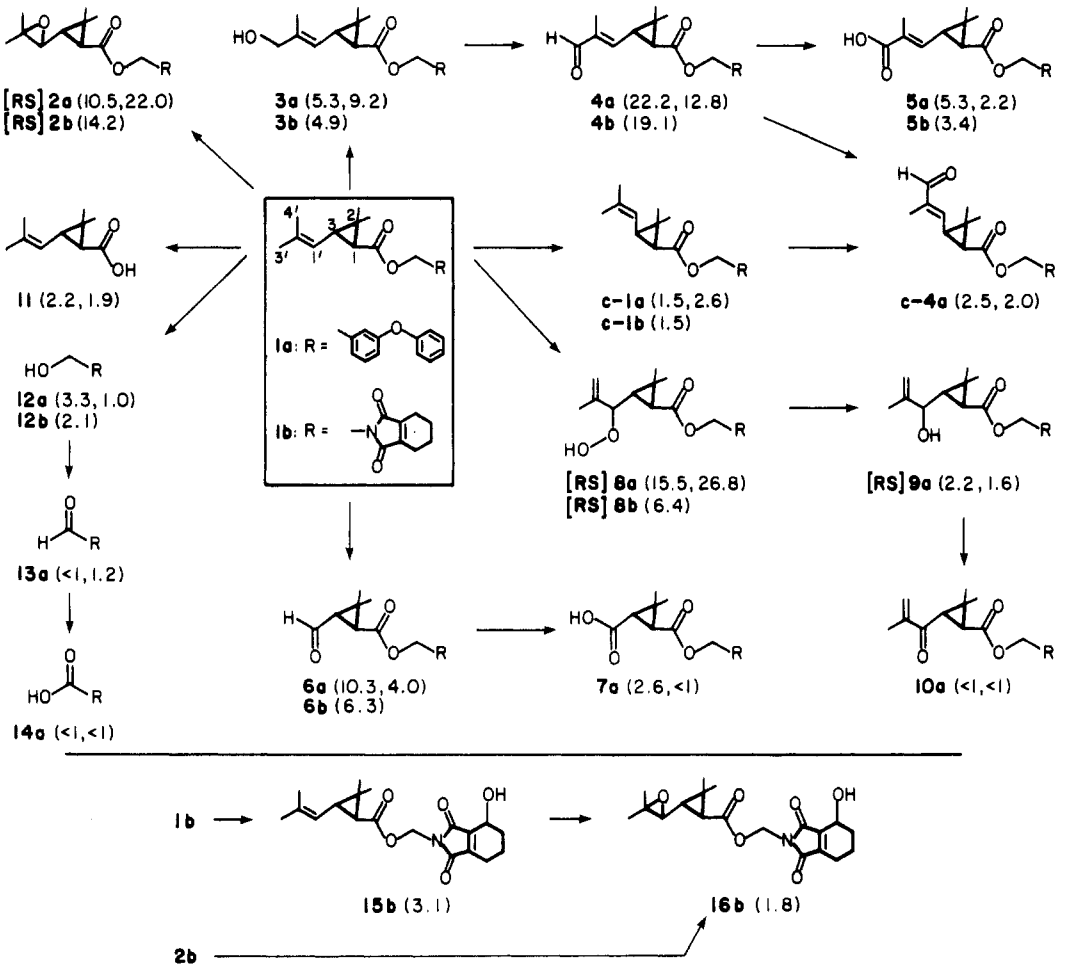

Figure 1. Photodecomposition pathways and yields for *trans*-phenothrin (**1a**) and *trans*-tetramethrin (**1b**). Yields are relative to the amount of starting material reacted at ~30% conversion, given first for the thin film and then for the oxygenated solution (**1a**) or for the thin film only (**1b**). Unidentified photoproducts of **1a** account for 16.6% as a thin film and 12.7% in solution and of **1b** account for 37.2% as a thin film. The general structure of the parent esters indicates the numbering used for carbons in the chrysanthemate moiety.

Aldehydes **4a** and *c*-**4a** were obtained by treatment of **1a** and *c*-**1a**, respectively, with 1.1 equiv of SeO_2 in refluxing dioxane (Matsui and Yamada, 1963). After 1 h the solution was cooled and decanted, and the soluble products were subjected to TLC (CE) to obtain **4a** or *c*-**4a** in >80% yield. Aldehyde **4b** was prepared by coupling the appropriate acid chloride with **12b** in benzene containing equivalent pyridine at reflux for 1 h. After the mixture was stirred overnight, extraction and TLC purification (CE) gave **4b** in 92% yield.

The methyl esters of **5a** (**5a**-Me) and **5b** (**5b**-Me) were obtained by coupling *trans*-pyrethric acid chloride with 1.2 equiv of **12a** or **12b** in benzene containing equivalent pyridine at reflux for 1 h (**5a**-Me) or at 25 °C overnight

(**5b**-Me). After extraction and TLC purification (CE), **5a**-Me and **5b**-Me were obtained in 72 and 90% yields, respectively.

Aldehydes **6a** and **6b** were synthesized from **1a** and **1b** (0.15 mmol) in hexane (10 mL) by flushing with ozone (O_3) (generated with a microozonizer; Supelco, Bellefont, PA) for 30 min and then addition of excess triphenylphosphine to decompose the ozonides. The aldehydes were obtained in 80–90% yield after TLC purification (HE). Acid **7a** (341, M + 1) was prepared by oxidation of **6a** with oxygen in dichloromethane. Treatment of **7a** with diazomethane yielded the methyl ester (**7a**-Me) quantitatively.

Hydroperoxides **8a** and **8b** as diastereomeric mixtures (1′*RS*) were synthesized by reaction of **1a** and **1b** (0.15 mmol) with singlet oxygen ($^1O_2$) generated by sunlamp irradiation of an oxygenated acetonitrile solution (10 mL) containing 1% rose bengal. The products were obtained in >90% yield; however, reaction of **1a** also yielded small amounts (~2%) of aldehyde **6a**. The hydroperoxides were purified by TLC (2 × HE) and gave characteristic colors with 4-(*p*-nitrobenzyl)pyridine and with starch–iodide test paper.

Alcohol (*RS*)-**9a** was prepared by reduction of (*RS*)-**8a** with excess $NaBH_4$ in ether at 20 °C. After the mixture was stirred overnight, water was added and the ether layer was chromatographed (CA). The diastereomeric mixture (1′*RS*) was derivatized with acetyl chloride to give (*RS*)-**9a**-OAc. Ketone **10a** was detected as a photoproduct but not synthesized.

Ester cleavage products **11**–**14** were from the following sources: **11** and **12b** from Sumitomo Chemical Co.; **12a**, **13a**, and **14a** from Roussel-Uclaf.

The diacetoxy intermediate for the alcohol moiety of **15b** and **16b** (Smith and Casida, 1981) was prepared by reacting *N*-(acetoxymethyl)-3,4,5,6-tetrahydrophthalimide (1.8 mmol) with SeO_2 (9 mmol) in glacial acetic acid (10 mL) at reflux overnight. The solvent was decanted and then removed under vacuum. The product was redissolved in ether and washed with water and saturated $NaHCO_3$. Purification by TLC (CA) gave *N*-(acetoxymethyl)-3-acetoxy-3,4,5,6-tetrahydrophthalimide in 22% yield: CI-MS 222 (M − 59, 53), 162 (9); NMR δ 2.05 (s, 3 H), 2.09 (s, 3 H), 5.82 (m, 1 H). This diacetate was dissolved in THF containing 10% 2 M H_2SO_4 and refluxed overnight. The solvent was removed under vacuum, and the mixture was taken up in saturated NaCl and extracted with ether. TLC purification (chloroform–acetone, 4:1) gave *N*-(hydroxymethyl)-3-hydroxy-3,4,5,6-tetrahydrophthalimide in 50% yield: CI-MS 180 (M − 17, 36), 107 (29); NMR δ 4.73 (m, 1 H), 5.05 (s, 2 H). Esterification on the primary alcohol was achieved with *trans*-chrysanthemoyl chloride in benzene containing equivalent pyridine. After the mixture was stirred overnight and chloroform was added, the mixture was washed with saturated $NaHCO_3$. TLC purification (chloroform–acetone, 4:1) gave **15b** in 22% yield: NMR δ 1.11 (s, 3 H), 1.26 (s, 3 H), 1.70 (s, 6 H), 1.90 (m, 4 H), 2.39 (m, 2 H), 4.85 (m, 2 H), 5.52 (m, 2 H). Epoxide **16b** was prepared by MCPBA oxidation of **15b** in dichloromethane.

Photolysis Procedures. For irradiations in the solid phase or as thin films, **1a** and **1b** (containing tracer levels of ^{14}C-labeled compound) were placed in Pyrex Petri dishes at 0.1–0.3 mg/cm^2. The dishes were covered with quartz plates and exposed to sunlight (Berkeley; September) for 30 and 2 h, respectively, at which time ~30% conversion had occurred. For preparative purposes photolyses were also carried out in a Rayonet reactor (The Southern New England Ultraviolet Co., Middleton, CT) equipped with RPR 3500 lamps. Individual photoproducts (**3a**, **4a**, and **6a**) were irradiated with sunlight (Berkeley; January).

In studies involving irradiation of solutions, compounds **1a**, **1b**, **4a**, and *c*-**4a** were photolyzed at 10^{-3} M in benzene (1 mL) in capped Pyrex tubes to 10–30% conversion by using RPR 3000 or RPR 3500 lamps. The solvent was either oxygenated by flushing for 2 h or degassed by three freeze–pump–thaw cycles at 0.01 mm. Additives were examined as follows: benzophenone, isobutyrophenone, and naphthalene (10^{-2} M); 1,4-diazabicyclo[2.2.2]octane (DABCO) and 2,5-dimethylfuran (10^{-3} M); 1,3-cyclohexadiene and anthracene (10^{-4} M).

Characterization of Photoproducts. Photolysis mixtures were divided into three portions. One was left untreated, the second was reacted with diazomethane, and the third was reacted with acetyl chloride–pyridine. TLC purification provided the photoproducts or their derivatives for characterization.

1a and its photoproducts were characterized by comparison with standards as follows: **1a**, (*RS*)-**2a**, **4a**, and *c*-**4a** by GLC, TLC, NMR, and CI-MS; **6a** and (*RS*)-**8a** by TLC, NMR, and CI-MS; **5a** and **7a** by methylation followed by comparison of the methyl esters with authentic materials by GLC, TLC, NMR, and CI-MS; **3a** and (*RS*)-**9a** by TLC, NMR, and CI-MS, and, following acetylation, by TLC, GLC, and CI-MS; *c*-**1a**, **12a**, and **13a** by GLC; **11** and **14a** by GLC following methylation. Compound **10a** was only tentatively characterized by GLC–CI-MS signals at 365 (M + 1, 4), 183 (100), and 165 (22). **1b** and its photoproducts were identical with standards as follows: **1b**, **3b**, and **4b** by TLC, NMR and CI-MS; **5b** by methylation followed by TLC, NMR, annd CI-MS; *c*-**1b**, (*RS*)-**2b**, **6b**, (*RS*)-**8b**, **12b**, **15b**, and **16b** by TLC and CI-MS. Epoxides (*RS*)-**2a** and (*RS*)-**2b** were further characterized with 4-(*p*-nitrobenzyl)-pyridine and hydroperoxides (*RS*)-**8a** and (*RS*)-**8b** with starch–iodide test paper and based on their IR bands (chloroform) at 3520 cm^{-1} (OH stretch).

Quantitation of Photoproducts. Photoproduct yields (Figure 1) are based on the amount of starting material reacted. The photoproducts of **1a** after suitable derivatization were quantitated by GLC sometimes following preliminary TLC cleanup. Compounds **6a** and (*RS*)-**8a** were exceptions, and due to partial decomposition on GLC they were isolated by TLC and their weight was determined after ether extraction. The photoproducts of **1b** or their derivatives from diazomethane treatment were quantitated by liquid scintillation counting following TLC separation. The yield of **12b** is an estimate based on weight recovery from TLC.

RESULTS

c-**1a** is the only product detected on irradiation of **1a** in degassed benzene at 360 nm. In contrast, a great variety of products are formed on irradiation of **1a** in oxygenated benzene solution at 360 nm, and the reaction rate is 5–10-fold faster.

Oxidation Reactions. A similar product distribution is obtained at ~30% conversion on photolysis of **1a** in oxygenated benzene solution at 360 nm and as a thin film in sunlight (Figure 1). The yields of individual photoproducts under these conditions are more dependent on the extent of conversion than on the reaction phase or irradiation source. Thus, with **1a**, the same photoproducts are obtained at 5 and 50% conversion as thin films but the relative proportions vary, i.e., more **5a** than **3a** at higher conversion. With **1b**, on the otherhand, the identified ester photoproducts account for ~80% yield at 5% conversion but only ~20% yield at 50–70% conversion

where more extensive decomposition is evident [much of the radiocarbon remains at the origin on TLC (CA; HT)]. This difference between **1a** and **1b** undoubtedly results from reactivity conferred by the *N*-(hydroxymethyl)-tetrahydrophthalimide moiety; e.g., this alcohol moiety is easily oxidized at the allylic methylene, forming **15b** and **16b**.

The major photoproducts of **1a** and **1b** are the epoxides (*RS*)-**2a** and (*RS*)-**2b**, the aldehydes **4a** and **4b** and **6a** and **6b**, and the allylic hydroperoxides (*RS*)-**8a** and (*RS*)-**8b** resulting from oxidation of the chrysanthemate moiety.

Further experiments were designed to establish the relative contribution of the theoretically possible routes to these products.

$^3O_2$ Reactions. Alcohols **3a**, **3b**, **15b**, and **16b** are probably formed by hydrogen abstraction at the allylic position followed by addition of ground-state oxygen to the newly created radical. Further oxidation of **3a** leads to **4a** and **5a** and of **3b** to **4b** and **5b**. $^3O_2$ reactions may also be a source of epoxides (*RS*)-**2a** and (*RS*)-**2b** since they exhibit diastereomeric character which tends to rule against O_3 involvement. Photooxidation of **1a** in benzene is partially quenched by alternate substrates such as 1,3-cyclohexadiene.

$^1O_2$ Reactions. Photolysis of **1a** and **1b** yields substantial amounts of the diastereomeric mixtures of allylic hydroperoxides [(*RS*)-**8a** and (*RS*)-**8b**] and of the caronaldehyde derivatives (**6a** and **6b**). Hydroperoxide (*RS*)-**8a** reacts further to give the allylic alcohol (*RS*)-**9a** and eventually trace amounts of ketone **10a**. Quenching of **1a** reactions in solution with 2,5-dimethylfuran or DABCO results in sharply decreased yields of (*RS*)-**8a** and, to a lesser extent, of (*RS*)-**2a** and **6a**.

O_3 Reactions. Aldehydes **6a** and **6b** are formed from **1a** and **1b** on treatment with ozone in solution. Photochemical formation of **6a** and **6b** does not result from ground-state ozonolysis since light is required to convert **1a** and **1b** to their caronaldehyde derivatives and for ozone formation. Further oxidation of **6a** gives the acid **7a**, in greater yields from solid phase than from solution irradiations.

Ester Cleavage Reactions. The acid and alcohol moieties of **1a** and **1b** are minor photoproducts under the irradiation conditions examined. *trans*-Chrysanthemic acid (**11**) is detected from **1a** and **1b** while 3-phenoxybenzyl alcohol (**12a**) undergoes further oxidation to the aldehyde (**13a**) and acid (**14a**). The only identified alcohol moiety product from **1b** is **12b**.

Sensitized Photolyses and Trans/Cis Isomerization. The cis isomers (c-**1a** and c-**1b**) are formed in small yield on irradiation of **1a** and **1b**. Another product previously observed on triplet reactions of dimethylcyclopropanecarboxylates, 3-phenoxybenzyl 2,2-dimethylacrylate (Holmstead et al., 1978), is not detected with **1a**. Formation of *c*-**1a** is considerably increased in deoxygenated benzene and in the presence of isobutyrophenone (E_t = 73 kcal/mol) or benzophenone (69 kcal/mol) while it is decreased by 1,3-cyclohexadiene (50 kcal/mol) or anthracene (42 kcal/mol).

Irradiation of aldehyde **4a** in solution or in the solid phase yields an *E*/*Z*,cis/trans isomer mixture separable on TLC followed by GLC (Table I). The recovered *c*-**4a** was an *E*/*Z* mixture (NMR). Isobutyrophenone-sensitized reaction of **4a** yields a photostationary mixture of (*E*)-**4a**/(*Z*)-**4a**/(*E*)-*c*-**4a**/(*Z*)-*c*-**4a** in the ratio 4:2:2:1; the cis/trans and *E*/*Z* isomerizations are equally quenched with 1,3-cyclohexadiene or anthracene. A photostationary mixture could not be obtained in the direct photolysis due to secondary reactions; e.g., longer irradiation times yield **5a** and its cis isomer (TLC). Photolysis of the *tert*-butyl ester of the acid moiety of **4a** also gave the anticipated isomer mixture evident by NMR (cis/trans) and GLC (*E*/*Z*,cis/trans).

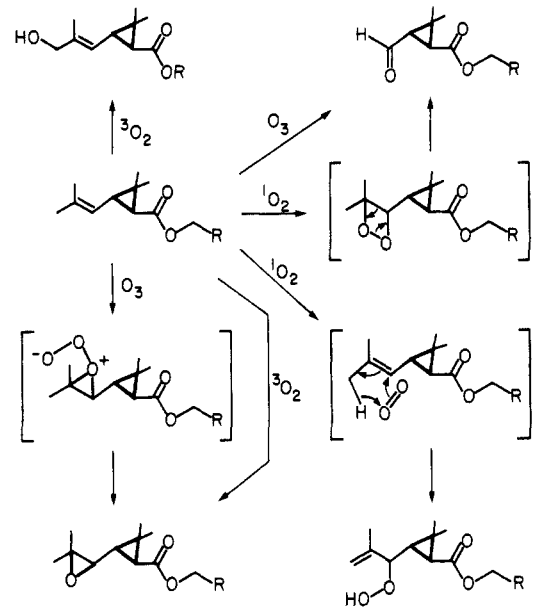

Figure 2. Possible photooxidation mechanisms of the chrysanthemate isobutenyl moiety involving singlet and triplet oxygen and ozone.

DISCUSSION

The chrysanthemate moiety of **1a** and **1b** is readily photooxidized, yielding derivatives analogous to previously suggested photoproducts of other pyrethroids (esters equivalent to **2**–**5** and **7**; Chen and Casida, 1969; Ueda et al., 1974; Ruzo et al., 1980) and additional derivatives shown in Figure 1. These reactions involve $^1O_2$, $^3O_2$, or O_3 (Figure 2). Further degradation of the initial photoproducts yields a very complex mixture of compounds, only a portion of which are identified, e.g., 3-phenoxybenzyl alcohol and the corresponding aldehyde and acid (Holmstead et al., 1978).

Epoxide (*RS*)-**2** formation results for the most part from $^3O_2$ addition. O_3 may also be partially responsible, although in this case some stereospecificity would be expected (Murray and Suzui, 1973). A contribution from $^1O_2$ is indicated by the quenching of epoxidation with $^1O_2$ traps and its involvement in *trans*-cyclooctene epoxidation (Inoue and Turro, 1980). The hydroperoxide (*RS*)-**8** may also act in turn as oxidant since certain α-substituted hydroperoxides epoxidize olefins (Rebek and McReady, 1980). Benzophenone increases the epoxide yield from *S*-bioallethrin (Ruzo et al., 1980) but not from **1a**.

Isobutenyl methyl oxidation involving $^3O_2$ yields a series of alcohol, aldehyde, and carboxylic acid derivatives probably formed at least in part by the **1** → **3** → **4** → **5** pathway. The aldehyde (**4**) appears in large amounts and in photomixtures at low conversion, suggesting either that the aldehyde is unusually stable under these conditions or that there is an alternative mechanism for its formation, e.g. by rearrangement or degradation of a primary hydroperoxide at the *E*-methyl group.

Hydroperoxides (*RS*)-**8a** and (*RS*)-**8b** are formed in considerable yields on ene reaction of **1a** and **1b** with $^1O_2$. The tertiary hydroperoxide containing unsaturation at C-3 of the cyclopropyl group, an alternative product from $^1O_2$ ene reactions, is not favored (Stephenson et al., 1980) and

is not detected. The identity of the oxidizing species is established by trapping with 2,5-dimethylfuran and by quenching with DABCO. In contrast, allethrin also reacts with $^1O_2$ in solution to give allylic hydroperoxides, but in this case they are not detected in exposed solutions or films (Ruzo et al., 1980). *endo*-Peroxide formation involves $^1O_2$ oxidation of the furan moiety with resmethrin (Ueda et al., 1974) and kadethrin (Ohsawa and Casida, 1979). $^1O_2$ formation in chrysanthemate photolysis probably results from sensitization by the pyrethroid or one of its photoproducts. These reactions are of particular interest because of the environmental importance of $^1O_2$ (Zepp et al., 1977).

Isobutenyl cleavage leading to the caronaldehyde (**6a** and **6b**) and caronic acid (**7a**) derivatives is probably initiated by light-mediated ozonolysis (Chen and Casida, 1969; Nambu et al., 1980). However, on photolysis in acetonitrile solution, $^1O_2$ addition may also be involved followed by disproportionation of the intermediate dioxetane.

Ester cleavage reactions of **1a** and **1b** probably do not result from triplet processes (Ruzo et al., 1980) but may be initiated by oxidative attack on the ester. Much greater yields obtained previously with allethrin may be related to the lower concentrations used in that study and the involvement of a secondary rather than a primary alcohol moiety.

Triplet trans/cis isomerization is an inefficient process with the chrysanthemate moiety of **1a** and **1b** in an oxygen-containing atmosphere as noted previously with allethrin (Ruzo et al., 1980). In contrast, the (*E*)-carboxaldehyde **4a** readily isomerizes on direct and sensitized photolyses, confirming an earlier observation for pyrethrates and related compounds (Ohsawa and Casida, 1979). Quenchers and sensitizers have an equal effect on both the cis/trans and *E*/*Z* interconversions of **4a**, indicating the involvement of a common excited state such as that formed by resonance stabilization across the cyclopropane bond as suggested for the thiolactone of kadethrin (Ohsawa and Casida, 1979).

Considerable progress has been made in defining the photolysis of the chrysanthemate moiety, but much remains to be learned about the photochemistry of the alcohol moieties of various chrysanthemate insecticides.

LITERATURE CITED

Casida, J. E.; Ruzo, L. O. *Pestic. Sci.* **1980**, *11*, 257.
Chen, Y.-L.; Casida, J. E. *J. Agric. Food Chem.* **1969**, *17*, 208.
Elliott, M.; Farnham, A. W.; Janes, N. F.; Needham, P. H.; Pulman, D. A.; Stevenson, J. H. *Proc. Br. Insectic. Fungic. Conf.* **1973**, *7*, 721.
Hammock, L. G.; Hammock, B. D.; Casida, J. E. *Bull. Environ. Contam. Toxicol.* **1974**, *12*, 759.
Holmstead, R. L.; Casida, J. E.; Ruzo, L. O.; Fullmer, D. G. *J. Agric. Food Chem.* **1978**, *26*, 590.
Inoue, Y.; Turro, N. J. *Tetrahedron Lett.* **1980**, *21*, 4327.
Matsui, M.; Yamada, Y. *Agric. Biol. Chem.* **1963**, *27*, 373.
Miyamoto, J.; Suzuki, T. *Pestic. Biochem. Physiol.* **1973**, *3*, 30.
Murray, R. W.; Suzui, A. *J. Am. Chem. Soc.* **1973**, *95*, 3343.
Nambu, K.; Ohkawa, H.; Miyamoto, J. *Nippon Noyaku Gakkaishi* **1980**, *5*, 177.
Ohsawa, K.; Casida, J. E. *J. Agric. Food Chem.* **1979**, *27*, 1112.
Rebek, J.; McReady, R. *J. Am. Chem. Soc.* **1980**, *102*, 5602.
Ruzo, L. O. In "Progress in Pesticide Biochemistry"; Hutson, D. H.; Roberts, T. R., Eds.; Wiley: New York, 1981; in press.
Ruzo, L. O.; Casida, J. E. *J. Chem. Soc., Perkin Trans 1* **1980**, 728.
Ruzo, L. O.; Gaughan, L. C.; Casida, J. E. *J. Agric. Food Chem.* **1980**, *28*, 246.
Smith, I. H.; Casida, J. E. *Tetrahedron Lett.* **1981**, *22*, 203.
Stephenson, L. M.; Grdina, M. J.; Orfanopoulos, M. *Acc. Chem. Res.* **1980**, *13*, 419.
Ueda, K.; Gaughan, L. C.; Casida, J. E. *J. Agric. Food Chem.* **1974**, *22*, 212.
Yamamoto, I.; Casida, J. E. *Agric. Biol. Chem.* **1968**, *11*, 1382.
Zepp, R. G.; Wolfe, N. L.; Baughman, G. L.; Hollis, R. C. *Nature (London)* **1977**, *267*, 421.

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