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Pyrethroid Photochemistry: Intramolecular Sensitization and Photoreactivity of 3-Phenoxybenzyl, 3-Phenylbenzyl, and 3-Benzoylbenzyl Esters

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Intramolecular sensitization is examined as a means to modify pyrethroid photostability by using a series of 3-phenoxybenzyl (**A**), 3-phenylbenzyl (**B**), and 3-benzoylbenzyl (**C**) esters of *cis*-chrysanthemic acid (**1**), *cis*-3-(2,2-dichloro- and -dibromovinyl)-2,2-dimethylcyclopropanecarboxylic acids (**2** and **3**), 2,2,3,3-tetramethylcyclopropanecarboxylic acid (**4**), and α-(4-chlorophenyl)isovaleric acid (**5**). Quantum yields in degassed benzene solutions irradiated at 300 nm are similar for **A** and **B** esters, whereas remarkable stability is encountered with **C** esters of **4** and **5** as a result of decreased ester cleavage, a reaction that proceeds by direct absorption rather than via triplet states populated by energy transfer. Esters of **C** with **1**, **2**, and **3** undergo greatly enhanced cis/trans isomerization due to intramolecular energy transfer. On exposure of thin films to sunlight the stability order is generally **A** > **B** > **C** as expected from their absorptivity and **4** > **5** > **2** > **3** > **1**, consistent with their absorptivity and ease of oxidation. Sunlight irradiation of **2** and **3** esters yields the trans isomers and ester cleavage materials as major products and the monohalovinyl derivatives and the caronaldehyde and caronic acid esters as minor products. The **C** moiety is stabilized to light without destroying the insecticidal activity on derivatization as the benzhydryl acetate.

Photostability is an important consideration in the design and use of pyrethroids for agricultural pest control. Photolabile substituents have been replaced with isosteric groups resistant to oxidation and other photoreactions, thereby conferring enhanced stability (Ruzo, 1982; Ruzo and Casida, 1980). Photoreactions might also be minimized by introducing substituents for radiative energy disposal or for intramolecular transfer of absorbed energy to nonreactive groups.

The photolability of chrysanthemates (**1**, Figure 1) is due in part to the ease of oxidation at the isobutenyl methyl group and double bond (Chen and Casida, 1969; Ruzo et al., 1980, 1982) that has been overcome by replacing the isobutenyl acid with dihalovinyl acids **2** and **3** [e.g., permethrin (**2A**) is much more stable than phenothrin (**1A**) (Elliott et al., 1973; Ruzo and Casida, 1980)]. Esters of **1** readily undergo cis/trans photoisomerization in the presence of acetophenone (E_t = 74 kcal/mol) and benzophenone (E_t = 69 kcal/mol) (Ruzo et al., 1982; Ueda and Matsui, 1971). Known photoreactions of esters derived from **2** and **3** are dominated by cis/trans isomerization and do not include oxidation of the dihalovinyl substituent (Holmstead et al., 1978a; Ruzo et al., 1977). Acid moiety **4**, present in fenpropathrin (Matsuo et al., 1976), is of interest because photochemical cleavage of the C1–C3 bond may yield a diradical that can recombine to regenerate the starting cyclopropanecarboxylate. Photodegradation of fenvalerate and analogues derived from acid moiety **5** is characterized by extensive decarboxylation (Holmstead et al., 1978b).

The phenoxybenzyl moiety (**A**) and its α-cyano analogue are present in the major pyrethroids permethrin, cyper-

methrin, deltamethrin, and fenvalerate. Phenylbenzyl and benzoylbenzyl moieties **B** and **C** also yield insecticidal esters, e.g., **2B** (Plummer and Pincus, 1981) and **2C** (Elliott and Janes, 1979; Plummer and Pincus, 1981). The biphenyl (E_t = 65 kcal/mol) and benzophenone chromophores in these compounds have triplet energies sufficient to profoundly influence cis/trans isomerization, decarboxylation, and ester cleavage reactions.

This study evaluates the effects of sensitizing chromophores on the photoreaction rates and photoproducts of a variety of pyrethroids derived from acid moieties **1–5** and alcohol moieties **A–C** (Figure 1).

MATERIALS AND METHODS

Chromatography and Spectroscopy. Thin-layer chromatography (TLC) utilized silica gel F-254 chromatoplates with 0.25- and 0.5-mm gel thickness for analytical and preparative purposes, respectively, and compound detection by quenching of gel fluorescence at 254 nm. High-pressure liquid chromatography (HPLC) was carried out on a μPorasil column (30 cm × 7.8 mm i.d.) eluted with chloroform–hexane (3:1) at 1–2 mL/min. UV absorption spectra were determined for compounds in chloroform solution.

Analysis. Gas–liquid chromatography (GLC) was accomplished in four systems: (A) an SP-2100 capillary column (Supelco, Bellefonte, PA) with helium carrier gas or (B) an OV-101/OV-210 (3% each) packed glass column with argon–methane (20:1) carrier gas, in each case in conjunction with a Hewlett-Packard 5840 chromatograph with [63]Ni electron capture detector and on-line computer to calculate retention times (R_t) and normalized peak areas; (C) a 5% OV-25 packed glass column with nitrogen carrier gas and a Varian Aerograph 1400 instrument with a flame ionization detector; (D) a 5% OV-101 column with methane as the carrier and ionization gas at 0.8 torr in conjunction with a Finnigan 9500 chromatography, a Finnigan

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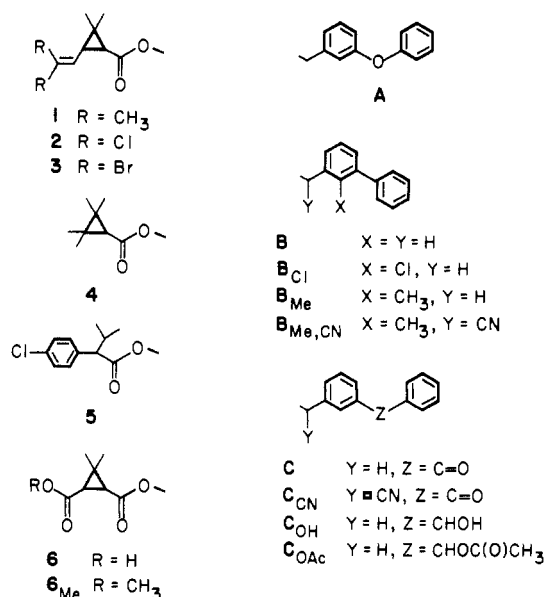
1 R = CH₃
2 R = Cl
3 R = Br

4

5

6   R = H
6ₘₑ R = CH₃

A

B   X = Y = H
B_Cl   X = Cl, Y = H
B_Me   X = CH₃, Y = H
B_Me,CN X = CH₃, Y = CN

C   Y = H, Z = C=O
C_CN   Y = CN, Z = C=O
C_OH   Y = H, Z = CHOH
C_OAc Y = H, Z = CHOC(O)CH₃

Figure 1. Acid (1-6) and alcohol (A-C) moieties of pyrethroids and their derivatives.

3200 chemical ionization mass spectrometer (CI-MS), and a System Industries Model 150 data system. For CI-MS on directly introduced samples the probe temperature was 40–220 °C and the ionization voltage was 40–70 eV. Compounds examined in each system were as follows (see paragraph at end of paper regarding supplementary material): (A) photoproduct mixtures derived from 4A, 5A, 4B, 5B, 4C, 5C, and 3C_CN; (B) photoproduct mixtures derived from 2B, 3B, 2B_Me, and 2C_OAc; (C) photoproduct mixtures derived from 1A, 2A, 3A, 2B_Cl, 2B_Me,CN, 1C, 2C, and 3C; (D) photoproduct mixtures in the solid phase derived from 2A, 2B, 3B, 2B_Cl, 2B_Me, 2C, 4C, and 5C and compounds designated as 6_MeA, 6_MeB, 6_MeB_Cl, 6_MeB_Me, 6_MeC, B-CH₂OH, B-CHO, B-CO₂Me, C-CH₂OH, C-CHO, and C-CO₂Me.

Chemicals. Figure 1 gives the number and letter designations used for various acid and alcohol moieties, respectively. Subscripts designate derivatives of the indicated acid and alcohol moieties; i.e., Cl = chloro, CN = cyano in the α or benzylic methine position, OAc = acetoxy, OH = hydroxy, and Me = methyl. Alcohol moieties are designated as, e.g., B-CH₂OH, B-CHO, and B-CO₂Me for the relevant alcohol, aldehyde, and acid methyl esters, respectively.

Acid Moieties. The following acids were utilized as standards or in synthesis: cis- and trans-1 (Sumitomo Chemical Co., Osaka, Japan); cis- and trans-2 and -3 (Roussel-Uclaf, Paris, France); 4 and 5 (Shell Development Co., Modesto, CA); caronic acid from ozonolysis of chrysanthemic acid (Ruzo et al., 1982) in dichloromethane followed by oxidation with KMnO₄ in acetone: CI-MS m/z (rel intensity) 159 (M + 1, 100), 187 (M + 29, 25).

Alcohol Moieties and Derivatives Thereof. A-CHO (Aldrich Chemical Co.) was reduced to A-CH₂OH with LiAlH₄ or oxidized to A-COOH with KMnO₄. B-COOH and C-COOH (ICN Pharmaceuticals) were converted to the acid chlorides (SOCl₂, reflux), which were reduced with lithium tri-tert-butoxyaluminum hydride in dry tetrahydrofuran to obtain B-CH₂OH and C-CH₂OH. The aldehydes were obtained by pyridinium chlorochromate oxidation of the alcohols in dry dichloromethane.

Pyrethroids and Other Esters. Pyrethroids obtained as gifts were cis- and trans-1A (Sumitomo), cis- and trans-2A (Roussel-Uclaf), 2B, 2B_Cl, 2B_Me, and 2B_Me,CN (FMC Corp.,

Middleport, NY), 3C_CN (N. F. Janes, Rothamsted Experimental Station, England), and 5A (Shell).

Pyrethroids 3A, 4A, 3B–5B and 1C–5C and their respective trans isomers (where applicable) were synthesized by coupling the acid chloride (SOCl₂) with the corresponding alcohol in benzene containing equivalent pyridine at reflux for 1–3 h. After extraction they were purified by TLC or HPLC. trans-6_MeB was obtained by treatment of trans-caronic acid with excess SOCl₂ for 3 h at reflux followed by evaporation and reaction of the dichloride with 0.5 equiv of B-CH₂OH in benzene containing equivalent pyridine. After 3 h of reflux the reaction was quenched with methanol, yielding the desired ester (TLC isolation). 1C_OH–5C_OH were prepared in an analogous manner by coupling acids 1–5 with C_OH-CH₂OH [CI-MS m/z (rel intensity) 214 (M, 0.5), 197 (M − 17, 100), 137 (85)] from LiAlH₄ reduction of 3-benzoylbenzoyl chloride. 2C_OAc was obtained by treatment of 2C_OH with acetyl chloride and pyridine in benzene.

Photolyses. *Solutions.* The pyrethroids (0.03 M) were irradiated in degassed benzene (spectrophotometric grade, Aldrich, redistilled) in stoppered Pyrex tubes mounted on a merry-go-round with a Rayonette photoreactor (The Southern New England Ultraviolet Co., Middletown, CT) equipped with RPR 3000 lamps. This concentration absorbed >80% of wavelengths below 310 nm. After preliminary surveys, the rates were measured by analyses of duplicate samples at each of three irradiation times, giving between 5 and 30% conversions, using either 2A or 2C as a comparison compound in each experiment. Quanta absorbed were measured (mean of three readings) with the cyclopentanone actinometer (Dunion and Trumbore, 1965; Ruzo and Casida, 1980).

Solids. The pyrethroids as thin films (75 nmol/cm²) in covered Pyrex Petri dishes were exposed to sunlight; similar results were obtained on irradiation with RPR 3500 lamps in the Rayonette reactor. After initial surveys, duplicate samples were irradiated for appropriate times to determine reaction rates. For consistency, all final results are for samples irradiated simultaneously. For identification of their photoproducts, 1C_OH–5C_OH, A-CH₂OH, B-CH₂OH, and C-CH₂OH were irradiated with sunlight for up to 8 h, 2C_OAc was irradiated for up to 15 days, and A-COOH was irradiated for 30 days, each as thin films at 500 nmol/cm².

Identification and Analysis of Photoproducts. Reactions were carried out to 5–30% conversion for rate studies with quantitation by GLC peak area comparisons with standards. All yields are based on total starting material consumed.

Product formation was examined in detail in the solid-phase reactions at 35–75% conversion by using GLC–CI-MS as previously indicated. The photoproduct mixtures were chromatographed (TLC) in the appropriate solvent systems before and after methylation (diazomethane). Characterization was based on TLC and GLC cochromatography and comparison of CI-MS quasimolecular ions (M + 1) and important fragments with those of authentic standards or solely by CI-MS. The acid moieties were identified by GLC–CI-MS cochromatography of their methyl esters with authentic materials. GLC, TLC, and CI-MS data for the relevant photoproducts and standards are given in the supplementary material.

RESULTS

Structure–Photoreactivity Relationships in Solution. The reactivities for the pyrethroids studied are derived from their quantum yields when irradiated at 300 nm in degassed benzene (Table I). Esters of 3 are

3-Phenoxybenzyl, 3-Phenylbenzyl, and 3-Benzoylbenzyl Esters

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Table I. Photoreactivity of 3-Phenoxy-, 3-Phenyl-, and 3-Benzoylbenzyl Esters in Benzene Irradiated at 300 Nanometers and as Thin Films Exposed to Sunlight

acid moiety	rel reactivity with indicated alcohol moiety[a]					
	benzene, 300 nm			thin film, sunlight		
	A	B	C	A	B	C
1	1.0^d		4.1^b	9.8^h		81^g
2	1.0^c	2.0^b	6.7^b	1.0^h	5.7^e	28^f
3	3.9^c	2.3^c	8.0^b	4.2^h	18^e	65^e
4	1.4	0.5	0.07	0.5	0.06	11
5	1.7	1.9	0.13	0.8	0.5	32

[a] Values are relative to those of 2A with a quantum yield in benzene of 1.5×10^{-3} and a reactivity as a thin film of 33 nmol cm^{-2} h^{-1}. Quantum yields in benzene ranged from $\sim 1 \times 10^{-4}$ for 4C to 1.2×10^{-2} for 3C. The reactivity of thin films ranged from 2 nmol cm^{-2} h^{-1} for 4B to 2.7 µmol cm^{-2} h^{-1} for 1C. [b-h] Trans isomer formed was (b) >99%, (c) 95-99%, (d) 90-95%, (e) 70-78%, (f) 44%, (g) 10-20%, and (h) 1-10%.

Table II. Effect of Benzyl Substituents on the Photoreactivity of 3-Phenylbenzyl and 3-Benzoylbenzyl cis-Dihalovinyldimethylcyclopropanecarboxylates

compd	benzyl substituents		rel reactivity[a]		% trans isomer formed, sunlight[b]
	X	Y	benzene, 300 nm	thin film, sunlight	
2B	H	H	2.0	5.7	76
2B$_{Cl}$	Cl	H	6.7	1.7	15
2B$_{Me}$	Me	H	3.5	1.2	16
2B$_{Me,CN}$	Me	CN	4.3	1.9	21
3C		H	8.0	65	78
3C$_{CN}$		CN	7.9	61	72

[a] See Table I, footnote a. [b] >99% trans isomer formed in benzene at 300 nm.

somewhat more reactive than their 1 and 2 analogues. The least reactive compounds are those where isomerization would not be detected, i.e., esters of 4 and 5, particularly with C. Reactivity differences associated with acid moiety substituents are much smaller for their A and B esters ($\sim$4-fold) compared to their C esters (114-fold), reflecting their respective sensitization efficiencies. Extinction coefficients (ϵ) at 290 nm reveal large differences between compounds containing the benzophenone chromophore and other pyrethroids, i.e., [compound (ϵ)] 1C (800), 3C (1360), and 4C (790) vs. 3B (306) and 4B (197) vs. 1A (50), 3A (252), and 4A (166). Substitution in the 2 position reduces absorptivity in the biphenyl series, i.e., 2B (219) vs. 2B$_{Cl}$ (97) and 2B$_{Me}$ (47). The α-cyano substituent does not greatly affect reactivity in either the phenylbenzyl compounds (2B$_{Me}$ vs. 2B$_{Me,CN}$) or the benzoylbenzyl series (3C vs. 3C$_{CN}$) (Table II). The 2 substituent in the biphenyl system enhances reactivity by 2-3-fold (Table II).

Structure–Photostability Relationships in Thin Films. Absorptivity differences were not adequately compensated in thin films, as was done in solution, so that the relative reactivities to a great extent reflect differences in light absorption as well as in intrinsic stability (Tables I and II). Thus, the reactivity order 1 esters > 3 esters > 2 esters differs from that in solution. The most stable compounds are those with acids 4 and 5 that resist oxidation and in which isomerization would not be detected. For alcohol moieties, the stability order is A > B > C for esters of 1-3 and B > A > C for esters of 4 and 5 (Table I). The α-cyano substituent does not alter the photostability, but the 2 substituents of B$_{Me}$ and B$_{Cl}$ retard the reactivity by 3-5-fold (Table II).

Identity of Ester Photoproducts. *Cis/Trans Isom-*
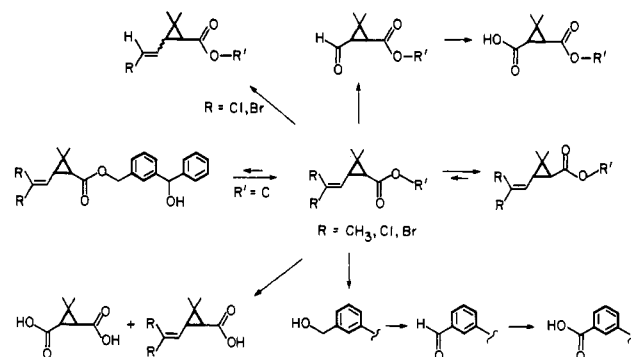
Figure 2. Photochemical pathways of pyrethroids examined.

erization in Solution and Solid-Phase Irradiations. The major reaction of the esters of 1, 2, and 3 in benzene at 300 nm at low conversions (<20%) is isomerization to the trans isomers. This process is somewhat more dominant for compounds with benzophenone and biphenyl chromophores relative to the phenoxybenzyl pyrethroids (Table I). Introduction of a 2 substituent in the phenylbenzyl series decreases the amount of isomerization observed in thin films (Table II). The only photoproducts identified in solution are the trans isomers of the cyclopropanecarboxylates. These trans isomers were also major photoproducts in the solid phase, with B and C as alcohol substituents.

Caronic Acid and Caronaldehyde Esters in Solid-Phase Irradiations and on Ozonolysis. Esters of caronic acid (6) were detected as photoproducts of 2A, 2B, 3B, 2B$_{Cl}$, 2B$_{Me}$, and 2C (Figure 2) in 5-10% yield except for 2A (<1%). They were tentatively identified by GLC-CI-MS after methylation and in the case of 6$_{Me}$B by GLC cochromatography with the authentic trans isomer. The dimethyl ester of caronic acid was always present as detected by GLC-CI-MS [187 (M + 1, 55)] and cochromatography (GLC) with the standard compound. The corresponding caronaldehydes (Figure 2) (identified by GLC-CI-MS) were obtained in $\sim$5% yield but only from the biphenyl compounds 2B and 3B; CI-MS m/z (rel intensity) 309 (M + 1, 6), 167 (100), 125 (15).

For determination of the possibility of ground-state reaction of the dihalovinyl substituent with ozone, 2$_{Me}$ (0.025 mmol) in dichloromethane (2 mL) was treated with ozone (2 h), yielding two major products after methylation of the reaction mixture (diazomethane) using GLC-CI-MS (system D, 90-120 °C) for detection and characterization. The caronaldehyde derivative [157 (M + 1, 11), 125 (100)] and the dimethyl ester of caronic acid [187 (M + 1, 40), 155 (100)] were obtained in 35 and 65% yields, respectively. When the reaction was carried out in the presence of a 50-fold excess of benzyl alcohol, dibenzyl carbonate was detected [135 (M - $C_6H_5CH_2O$, 15), 107 ($C_6H_5CH_2O$, 100)], indicating formation of phosgene during cleavage.

Other Ester Photoproducts. A minor product (<1%) obtained from 2A, 2B, and 3B is the reductively dehalogenated ester reported previously for permethrin (Holmstead et al., 1978a) and deltamethrin (Ruzo et al., 1977; Ruzo and Casida, 1980): for monochloro-2A, 357 (M + 1, 4), 183 (100), and 157 (9); for monochloro-2B, 341 (M + 1, 2), 167 (100), and 157 (14); for monobromo-3B, 429 (M + 1, 2), 201 (16), and 167 (100).

The benzhydryl esters were obtained from each of the benzoylbenzyl esters (TLC cochromatography); quantitation by GLC (systems A and B as the acetate) revealed 2% formation of 2C$_{OH}$ from 2C. The benzhydryl ester in turn was susceptible to photooxidation to the benzoylbenzyl ester, as shown with each of the five acid moieties exam-

ined, also yielding the corresponding trans isomers of 1C–3C. In contrast, 2C$_{OAc}$ does not yield 2C and reacts at a >200-fold slower rate than 2C$_{OH}$ when exposed to sunlight as a thin film. The toxicities of 2C, 2C$_{OH}$, and 2C$_{OAc}$ in topical tests with houseflies were found to be within 1 order of magnitude. All the compounds could be synergized more than 10-fold with piperonyl butoxide (300 μg/g applied 3 h before the pyrethroid).

Ester Cleavage Reactions and Photoproducts of Alcohol Moieties. Major products (>10%) at 35–75% conversion of thin films of 2A, 2B, 3B, 2B$_{Cl}$, 2B$_{Me}$, 2C, 4C, and 5C arise from ester cleavage reactions, giving the free acid moiety (40–80% yield; characterized by GLC–CI-MS as their methyl esters) and the corresponding alcohol, aldehyde, and acid from the aryl substituent (70–100% overall yield) (Figure 2).

Compounds B-CH$_2$OH and C-CH$_2$OH convert readily as thin films to the corresponding aldehydes and acids (detected as methyl esters) (Figure 2). The acids are formed early in the course of the reaction, suggesting considerable photoreactivity for the aldehydes. The benzoyl compound (C-CH$_2$OH) reacted ∼5-fold faster than the phenoxy compound (A-CH$_2$OH).

When A-COOH [a photoproduct and metabolite of several pyrethroids (Roberts, 1982; Ruzo, 1982)] is exposed to sunlight as a thin film for 30 days (5% conversion), the major product (GLC–CI-MS) is phenyl 3-phenoxybenzoate [291 (M + 1, 80), 197 (100)]. Minor products obtained after methylation of the reaction mixture (GLC) are anisole, methyl benzoate, and methyl 3-methoxybenzoate.

DISCUSSION

The photoreactions of pyrethroids are dependent on substituents absorbing light and intramolecularly transferring this energy to photolabile portions of the molecule. These factors lead to reactivity differences in sunlight of 1000-fold just within the few examples given in the present report. Even simple isomerization reactions are of practical importance since pyrethroid potency is critically dependent on stereochemical configuration.

The quantum yields of the pyrethroids examined are dependent largely on the efficiency of intramolecular energy transfer leading to C1–C3 bond isomerization. Thus, a comparison of esters with acid moieties undergoing cis/trans isomerization (1–3) with those where this does not occur (4, 5) reveals only a 4-fold difference in reaction rate with A and B alcohols without efficient sensitizers in contrast to a 32–114-fold difference with benzophenone-substituted C. Esters from bromo-substituted acids undergo isomerization somewhat faster than their chloro analogues, probably because of more accessible triplet excited states (Ruzo and Casida, 1980). The cyano substituent does not significantly affect the rate, confirming earlier findings (Ruzo and Casida, 1980). An ortho substituent in the biphenyl system increases the photoreactivity and yield of the trans isomer, probably because it increases the strain of the planar triplet biphenyl (Ruzo et al., 1974), resulting in a more efficient sensitizer due to higher triplet energies. On sunlight irradiation the 2 substituent of B lowers the reactivity by decreasing the absorptivity relative to that of the unsubstituted compound.

The reactivities of pyrethroids in thin films are determined to a major extent by their absorptivity and to a lesser extent by their ease of oxidation with a minor contribution from carbon–halogen bond strength. The high absorptivity of the benzoylbenzyl compounds undoubtedly accounts for their high level of reactivity both in isomer-

ization (esters of 1, 2, and 3) and in other reactions (esters of 4 and 5). On a similar basis the phenylbenzyl compounds are more reactive than the phenoxybenzyl esters. The structure is stabilized on removing the benzophenone chromophore (e.g., C$_{OAc}$ derivatives) in a form that is still of high insecticidal activity, potentially undergoing metabolic conversion back to the benzophenone.

Photocleavage of the vinyl substituent to give the caronaldehyde and caronic acid derivitives was noted previously with chrysanthemates (Nambu et al., 1980; Ruzo et al., 1982) but not with dihalochrysanthemates (Holmstead et al., 1978a; Ruzo et al., 1977). This cleavage probably involves ozonolysis (Figure 2) as also noted with other halogenated vinyls releasing dihalocarbonyls (Griesbaum and Brüggemann, 1972).

Ester cleavage continues to be the dominant photoreaction over long-term irradiations. For effective control of degradation, this process must be quenched or the energy it requires directed to an unreactive portion of the molecule. The present study shows that this can be accomplished with energy donors that do not interact with the carboxyl excited state, e.g., the phenylbenzyl and benzoylbenzyl substituents.

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