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Dinitroanilines as Photostabilizers for Pyrethroids

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A variety of 4-substituted 2,6-dinitroanilines stabilize pyrethroids to photodecomposition as thin films on silica gel or glass based on chemical analyses and bioassays. The 12 pyrethroids stabilized in this way include the pyrethrins, allethrin, kadethrin, resmethrin, tetramethrin, and cyphenothrin. Highly effective stabilizers of this type include trifluralin and its analogues with 1-propylamino, 1-amino, 4-methylsulfonyl, 4-sulfamoyl, and 4-dimethylsulfamoyl substitutents. These dinitroanilines are more effective stabilizers than 4-nitrophenol, 8-hydroxyquinoline, phenothiazine, and 104 other compounds examined. A cyphenothrin–trifluralin (5:1) mixture is as photostable as cypermethrin on silica gel. The photostability of cyphenothrin on silica gel or in solution is enhanced by 1 part of trifluralin or its 1-amino analogue to 10 000 parts of pyrethroid. The photoquenching action of the dinitroanilines at high ratios involves competition for light, but at very low ratios they may complex with the excited state of the pyrethroid.

The photostability of the pyrethrins and the synthetic pyrethroids has been improved in two ways. Photostabilizers including antioxidants and ultraviolet (UV) screens extend the effective life of photolabile compounds such as the chrysanthemates (Abe et al., 1972; Blackith, 1952; Chen and Casida, 1969; Glynne Jones, 1960; Miskus and Andrews, 1972; Pieper and Rappaport, 1982; Tattersfield and Martin, 1934; Ueda et al., 1974; Warner, 1963). Alternatively, the photolabile sites are replaced with more stable and usually halogenated groups to obtain structurally modified and photostabilized pyrethroids (Elliott and Janes, 1978; Miyamoto et al., 1981; Ruzo, 1982, 1983). The photostabilizer approach has potential advantages in improving the cost effectiveness of established compounds, in maintaining the favorable toxicology of chrysanthemates and nonhalogenated pyrethroids, and in controlling persistence as desired for specific control situations by varying the photostabilizer or its concentration. This potential has not been realized, in part due to the lack of photostabilizers of adequate effectiveness. We have therefore continued to search for improved photostabilizers for chrysanthemates and other insecticides.

MATERIALS AND METHODS

Chemicals. The pyrethroids examined were as follows: a 40% pyrethrins I and 46% pyrethrins II mixture referred to as "pyrethrins" and *S*-bioallethrin from McLaughlin Gormley King Co., Minneapolis, MN; (1*RS*)-*cis*-resmethrin of >98% purity from S. B. Penick & Co., Orange, NJ; (1*RS*)-*trans*-tetramethrin and (1*RS*,α*RS*)-*cis*-cyphenothrin of >95% purity from Sumitomo Chemical Co., Osaka, Japan; (*RS*)-fenpropathrin and (*SS*)-fenvalerate of >95% purity from Shell Development Co., Modesto, CA; kadethrin, (1*S*)-*cis*-phenothrin, (1*R*)-*cis*-permethrin, (1*R*,-α*S*)-*cis*-cypermethrin, and deltamethrin of >98% purity from Roussel Uclaf, Paris, France. Structures for these pyrethroids are given by Casida et al. (1983). [^{14}C]Cyphenothrin (2.7 mCi/mmol) was prepared by coupling (1*R*)-*cis*-[1-^{14}C]chrysanthemoyl chloride (Ueda et al., 1974) and (*RS*)-α-cyano-3-phenoxybenzyl alcohol (Ruzo et al., 1977) with pyridine in benzene and purification by thin-layer chromatography (TLC) (silica gel, carbon tetrachloride–ether, 3:1, R_f 0.56).

Pesticide chemicals were obtained from the basic manufacturers or the Health Effects Research Laboratory, U.S. Environmental Protection Agency (Research Triangle Park, NC). The procedure of Hall and Giam (1972) was used to react 4-chloro-3,5-dinitrobenzotrifluoride (Aldrich Chemical Co., Milwaukee, WI) with *n*-propylamine to obtain the monopropylamino analogue of trifluralin (mp 55–58 °C) and with ammonium hydroxide to obtain the amino analogue of trifluralin (mp 141–144 °C). The corresponding phenol was made by refluxing a mixture of chlorodinitrobenzotrifluoride and equimolar Na_2CO_3 in water for 24 h, cooling and acidification with HCl, filtration and washing the crystals with ether, and recrystallization from methanol (mp 208 °C). The methyl ether was obtained by treating the phenol in ether with diazomethane and crystallization from methanol (mp 40–41 °C). These trifluralin analogues gave appropriate mass spectra and nuclear magnetic responance spectra. Other chemicals used were from commercial sources.

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Radiochemical Analysis of [^{14}C]Cyphenothrin Photostabilization. More than 100 unlabeled pesticides and other chemicals with a wide variety of functional groups were surveyed as possible photostabilizers for [^{14}C]cyphenothrin. The radiolabeled compound facilitated analysis with the diversity of chemicals considered. A mixture of 10 μg each of [^{14}C]cyphenothrin and the candidate photostabilizer in ether was applied as a spot (10-mm diameter) at the origin of a silica gel chromatoplate (0.25-mm gel thickness, silica gel 60 without fluorescent indicator, E. Merck, Darmstadt, West Germany; prewashed with methanol). A 20 × 20 cm chromatoplate with six spots was placed in a Rayonet photochemical reactor (The Southern New England Ultraviolet Co., Middletown, CT) and irradiated with 12 RPR-3500A lamps (360-nM maximum energy output) for 24 h. The chromatoplate was then developed with carbon tetrachloride–ether (3:1, two developments) or carbon tetrachloride–toluene (1:1, two developments), giving R_f values for cyphenothrin of 0.81 and 0.38, respectively. Radioautography was used to detect [^{14}C]cyphenothrin as the applied (1*R*,α*RS*)-cis isomer mixture or possibly as a photoisomerized (1*RS*,α*RS*)-cis,trans isomer mixture. The labeled gel region was scraped into a scintillation vial for direct quantitation by liquid scintillation counting.

Gas–Liquid Chromatographic (GLC) Analysis of Pyrethroid Photostabilization. GLC analysis was used for studies varying the pyrethroid, photostabilizer ratio, and irradiation time. The unlabeled pyrethroid and candidate photostabilizer were combined, spotted, and irradiated as above. The photolysis mixtures were recovered from the silica gel by extracting with ether (2 mL). They were analyzed by adjusting the volume to 5 mL and GLC of a 2-μL aliquot with a Hewlett-Packard 5830A instrument fitted with a nickel-63 electron capture detector and a glass column (1.5 m × 4 mm i.d.) packed with GHP (80–100 mesh) coated with 5% OV-101. The carrier gas was 5% methane–95% argon with a flow rate of 30 mL/min. The inlet, column, and detector temperatures were 250 °C. Quantitation was provided by comparing the GLC peak area of the standard solution spotted on the silica gel with that of the parent compound recovered from the photodegraded mixture, with correction for 95% recovery. The retention times (min) were as follows: 1.88 and 2.22 for the two major peaks of the pyrethrins, 1.41 for allethrin, 2.23 for kadethrin, 1.35 for resmethrin, 3.21 for tetramethrin, 2.56 for phenothrin, 3.96 for cyphenothrin, 2.92 for fenpropathrin, 3.72 for permethrin, 6.22 for cypermethrin, 9.47 for deltamethrin, 8.19 for fenvalerate, and 0.96 for 3-phenoxybenzaldehyde. The possible presence of 3-phenoxybenzaldehyde was confirmed by using the same conditions except with a temperature program (150–250 °C, 6.7 °C/min, retention time 2.80 min).

Other Chemical Analyses. The possible formation of epoxides was examined by irradiation (360 nM, 18 h) of four pyrethroids (500 μg of allethrin, resmethrin, kadethrin, or cyphenothrin) alone or with trifluralin (100 μg) as spots (10 mm) at the origin of a silica gel chromatoplate. Cyphenothrin and cyphenothrin epoxide were separated on development with carbon tetrachloride–ether (3:1, two developments) (R_f 0.81 and 0.64, respectively) and carbon tetrachloride–toluene (1:1, two developments) (R_f 0.38 and 0.21, respectively). Cyphenothrin epoxide and putative epoxides from the other pyrethroids, separated with the same solvent systems, were detected with the 4-(*p*-nitrobenzyl)pyridine reagent (Hammock et al., 1974).

Bioassay Analysis of Pyrethroid Photostabilization. In one study a mixture of the pyrethroid (1–100 μg) and candidate photostabilizer (1 part to 5 parts of pyrethroid) was introduced as a thin film into a Petri dish (11-cm diameter) and irradiated for 4 h at 360 nM. Adult female houseflies were then added for 24-h mortality determinations and calculation of LD_{50} doses. A second experiment differed only in using 1000 μg of pyrethroid and 10 μg of trifluralin with irradiation for 8 h before introducing the flies.

Table I. Survey of 117 Potential Photostabilizers for [^{14}C]Cyphenothrin on Silica Gel with One Part of Cyphenothrin to One Part of Additive Irradiated for 24 h at 360 nM

type of compound	examples of photostabilizers and cyphenothrin recoveries, %
High Effectiveness, 75–100%	
2,6-dinitroanilines	trifluralin and eight 1- or 4-substituted analogues, pendimethalin
nitrophenols and nitrophenyl ethers	4-nitrophenol, 4-nitrocatechol, 4-nitroacetophenone, 2-nitrophenetole, nitrofen
acetophenones	3-amino, 3-hydroxy, and 2,4-dihydroxy derivatives
other	phenothiazine, 8-hydroxyquinoline, azobenzene
Moderate Effectiveness, 40–74%	
nitrophenols and nitrophenyl ethers	2-nitrophenol, chlomethoxynil
ketones and quinones	hydroxyquinone, chloranil, acetophenone, 2-hydroxybenzophenone
amines	diphenylamine, triphenylamine
other	4-cyanophenol, parathion, piperonyl butoxide, coumaphos, carbazole, benzimidazole, tetramethrin, rotenone, chlorobenzilate, phenylthiourea
Little or No Effectiveness, <39% Recovery	
other	78 other compounds[a] (<39% recovery) and no additive (~10% recovery)

[a] These compounds are identified in the supplementary material.

RESULTS

Survey of Potential Photostabilizers for Cyphenothrin on Silica Gel. Thirty-nine of 117 compounds tested stabilize [^{14}C]cyphenothrin against photodecomposition with one part of additive to one part of cyphenothrin [Table I and a supplementary table (see paragraph at end of paper regarding supplementary materials)]. This survey focused attention on 2,6-dinitroanilines, nitrophenols, and nitrophenyl ethers, acetophenones, phenothiazine, 8-hydroxyquinoline, and azobenzene for high effectiveness with some additional ketones, quinones, or amines and other compounds for moderate effectiveness.

The superiority of trifluralin as a photostabilizer is established by comparisons of trifluralin, 4-nitrophenol, phenothiazine, and 8-hydroxyquinoline as a function of irradiation time and photostabilizer ratio with GLC for cyphenothrin analysis (Table II). Trifluralin is highly effective since the photostability of a cyphenothrin–trifluralin mixture (5:1) on silica gel is equal to that of cypermethrin alone (Figure 1).

Cyphenothrin (5 parts) is photostabilized by trifluralin (1 part) on silica gel without fluorescent indicator when irradiated by sunlight as well as by the 360 nM lamp, i.e., cyphenothrin recoveries on 12-h sunlight irradiation of 18 ± 3% alone and 93 ± 2% with trifluralin. The use of silica gel chromatoplates with F254 fluorescent indicator does

Table II. Comparative Effectiveness of Four Photostabilizers for Cyphenothrin on Silica Gel Irradiated at 360 nM

compound	cyphenothrin recovery, %[a] 2 h	18 h	48 h
Irradiation Time Varied with Cyphenothrin:Photostabilizer Ratio of 5:1			
no photostabilizer	48 ± 3	7 ± 3	0.3 ± 0.6
trifluralin	93 ± 1	86 ± 2	60 ± 8
4-nitrophenol	90 ± 1	72 ± 3	42 ± 1
phenothiazine	92 ± 1	69 ± 3	37 ± 7
8-hydroxyquinoline	89 ± 1	71 ± 2	30 ± 4

compound	cyphenothrin recovery, %[b] 3:1	10:1	100:1
Cyphenothrin:Photostabilizer Ratio Varied with Irradiation Time of 12 h[b]			
trifluralin	90 ± 2	86 ± 1	73 ± 3
4-nitrophenol	91 ± 2	77 ± 3	67 ± 4
phenothiazine	89 ± 3	72 ± 4	54 ± 8
8-hydroxyquinoline	90 ± 0	79 ± 2	67 ± 3

[a] Average and standard deviation based on GLC analysis of three replicates. [b] Cyphenothrin recovery 22 ± 3% without stabilizer.

Table III. Trifluralin as a Photostabilizer for Various Pyrethroids on Silica Gel with Five Parts of Pyrethroid to One Part of Trifluralin Irradiated at 360 nM

pyrethroid	pyrethroid recovery, %[a] control	trifluralin
Pyrethroids with Nonhalogenated Acid Moieties Irradiated for 18 h		
pyrethrins	1 ± 0.5	54 ± 1
allethrin	2 ± 0.5	78 ± 3
kadethrin	0 ± 0	47 ± 3
resmethrin	7 ± 1	85 ± 4
tetramethrin	2 ± 0.5	77 ± 1
phenothrin	29 ± 1	66 ± 1
cyphenothrin	10 ± 1	89 ± 1
fenpropathrin	28 ± 2	83 ± 1
Pyrethroids with Halogenated Acid Moieties Irradiated for 32 h		
permethrin	32 ± 2	65 ± 1
cypermethrin	19 ± 5	83 ± 10
deltamethrin	25 ± 2	57 ± 4
fenvalerate	23 ± 2	90 ± 2

[a] Average and standard deviation based on GLC analysis of three replicates.

not significantly alter the photostability of cyphenothrin or the stabilizing effect of trifluralin with irradiation at 360 nM.

Trifluralin as a Photostabilizer for Various Pyrethroids. Trifluralin at 1 part to 5 parts of pyrethroid provides a very large stabilization factor for each of eight pyrethroids with nonhalogenated acid moieties irradiated on silica gel for GLC analysis (Table III) or on glass for housefly bioassay (Table IV). This stabilization also extends to four pyrethroids with halogenated acid moieties irradiated on silica gel based on GLC analysis (Table III).

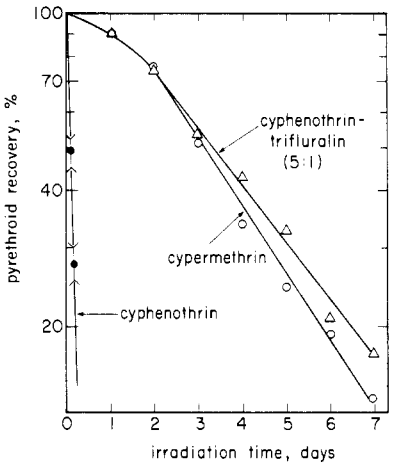

Figure 1. Comparative persistence of cyphenothrin, a cyphenothrin–trifluralin (5:1) mixture, and cypermethrin on silica gel irradiated at 360 nM. Data from GLC analysis are means of three replicates with standard deviations averaging 5% of the mean.

4-Substituted 2,6-Dinitroanilines and Related Compounds as Photostabilizers for Various Pyrethroids. Trifluralin and several of its analogues stabilize pyrethrins, allethrin, resmethrin, and cyphenothrin to photodecomposition on silica gel and/or glass with highest activity when the 1-substituent is amino or substituted amino rather than methoxy or hydroxy and when the 4-substituent is trifluoromethyl, methylsulfonyl, dimethylsulfamoyl, or sulfamoyl rather than isopropyl (Table V). Trifluralin and its 1-amino analogue are equally effective in stabilizing cyphenothrin on silica gel and show some stabilizing activity even at 1 part of dinitroaniline to 10 000 parts of cyphenothrin (Figure 2).

Preliminary bioassay experiments, which are not detailed here, revealed that the high effectiveness of the amino derivative of trifluralin as a photostabilizer for resmethrin on glass does not extend to treated cotton leaves exposed to sunlight.

Effect of Trifluralin on the Photodecomposition Pathways of Various Pyrethroids. Trifluralin stabilizes a variety of pyrethroids to photodecomposition with a 1:5 trifluralin–pyrethroid ratio (Tables III and IV). Epoxycyphenothrin is a prominent photoproduct of cyphenothrin on silica gel without trifluralin but is not evident with trifluralin (1:5 ratio). Trifluralin under these conditions also prevents the normal conversion of allethrin, resmethrin, and kadethrin to single major photoproducts of

Table IV. Trifluralin as a Photostabilizer for Five Pyrethroids on Glass with Five Parts of Pyrethroid to One Part of Trifluralin Irradiated for 4 h at 360 nM

pyrethroid	approximate housefly LD_{50}, μg/plate[a] dark	irradiated alone	irradiated with trifluralin	stabilization factor, LD_{50} alone/with trifluralin
pyrethrins	12	>500	25	>20
allethrin	2	180	5	36
resmethrin	1	300	3	100
kadethrin	2	500	3	167
cyphenothrin	2	150	4	38

[a] Photolysis of 1, 3, 10, 30, or 100 μg of pyrethroid for 4 h on glass and then bioassay with three replicates of 10 flies for each pyrethroid dose. LD_{50} values of >100 μg/plate are extrapolated data.

Table V. 4-Substituted 2,6-Dinitroanilines and Related Compounds as Photostabilizers for Four Pyrethroids on Glass or Silica Gel with 100 Parts of Pyrethroid to 1 Part of Photostabilizer Irradiated for 8 or 18 h at 360 nM

compound[a]			photodegraded residue[b]			
	substituents		pyrethroid recovery, %[c]		housefly mortality, %[d]	
no.	1	4	allethrin	cyphenothrin	allethrin and pyrethrins	cyphenothrin and resmethrin
1	Pr_2N	CF_3	53 ± 1	70 ± 4	68 ± 7	79 ± 8
2	Pr_2N	SO_2Me	54 ± 1	77 ± 2	73 ± 7	83 ± 7
3	Pr_2N	SO_2NMe_2	54 ± 3	81 ± 6	81 ± 5	92 ± 5
4	Pr_2N	SO_2NH_2	53 ± 5	80 ± 4	73 ± 9	79 ± 20
5	Pr_2N	*i*-Pr	35 ± 2	59 ± 2	34 ± 10	54 ± 12
6	PrNH	CF_3	51 ± 1	71 ± 1	58 ± 7	73 ± 5
7	NH_2	CF_3	54 ± 3	78 ± 3	63 ± 12	76 ± 6
8	CH_3O	CF_3	23 ± 4	44 ± 3	37 ± 6	49 ± 6
9	HO	CF_3	29 ± 6	48 ± 5	33 ± 9	46 ± 7
no photostabilizer			0	3 ± 3	0	2 ± 2

[a] Common names for dinitroanilines including herbicides are trifluralin (1), nitralin (2), dimethyloryzalin (3), oryzalin (4), isopropalin (5), and the monopropylamino (6) and amino (7) analogues of trifluralin. [b] Photolysis of 10 μg of pyrethroid for 18 h on silica gel for GLC analysis or 1000 μg of pyrethroid for 8 h on glass for bioassay. [c] Average and standard deviation based on three replicates. Recovery values were 95–100% for comparable samples of pyrethroids held 18 h in the dark. [d] Average and standard deviation for three replicates of 20 flies for each pyrethroid with pooled data since similar findings were obtained for allethrin and pyrethrins and for cyphenothrin and resmethrin. Comparable samples of pyrethroids held 8 h in the dark gave 100% mortality.

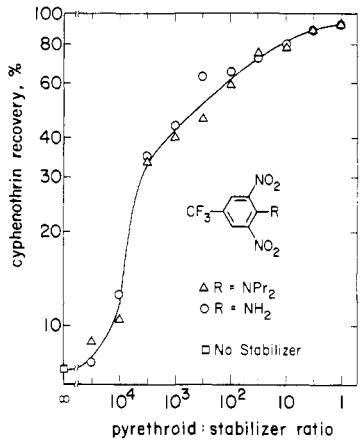

Figure 2. Trifluralin and its 1-amino analogue as photostabilizers for cyphenothrin with various pyrethroid:stabilizer ratios on silica gel irradiated at 360 nM. Data from GLC analysis are means of three replicates with standard deviations averaging 5% of the mean.

lower R_f and giving a blue color with 4-(*p*-nitrobenzyl)-pyridine reagent probably due to the corresponding epoxides. Loss of cyphenothrin on irradiation is associated with detection of 3-phenoxybenzaldehyde, a product not evident on irradiation of a cyphenothrin–trifluralin (5:1) mixture. Phenoxybenzaldehyde formation involves photolytic ester cleavage and decomposition of the liberated α-cyano-3-phenoxybenzyl alcohol on GLC; the aldehyde itself is photolabile and does not accumulate on irradiation of cyphenothrin.

Competitive Light Absorption by Cyphenothrin and Trifluralin or Its Amino Analogue. Solution phase photolyses and absorption spectra revealed that pyrethroid stabilization occurring at 1:1 or 5:1 pyrethroid:dinitroaniline ratios is due to competitive light absorption but that enhanced stability at 1000:1 or 10000:1 ratios is probably due to other characteristics of the photoquenchers. Thus, cyphenothrin is extensively photodecomposed when irradiated as a solution in hexane (0.1 mg/mL, 5% light absorption at 330–360 nM) for 24 h at 360 nM, but this photodecomposition is greatly retarded on addition of 1 part of trifluralin to 1000 or 10 000 parts of cyphenothrin. With the 1:1 mixture of cyphenothrin and trifluralin or its amino analogue in methanol, the dinitroanilines absorb at least 97% of the light at 330 and 360 nM. With a 5:1 mixture, the dinitroanilines absorb ~90% of the light under these conditions. However, at the 1000:1 ratio trifluralin in methanol absorbs <0.1% of the light at 330 and 360 nM and its amino analogue absorbs <0.5% of the light at 330 and ~1% at 360 nM.

DISCUSSION

Many compounds of high photostabilizing activity for pyrethroids have an aromatic ring with one or more electron-withdrawing groups and one or more electron-donating groups ortho or para to an electron-withdrawing group. The most effective photostabilizers examined are 2,6-nitroanilines, i.e., analogues and derivatives of trifluralin with an electron-withdrawing group in the 4-position (i.e., trifluoromethyl, methylsulfonyl, sulfamoyl, or dimethylsulfamoyl) and an electron-donating group in the 1-position (i.e., dipropylamino, propylamino, amino, methoxy, or hydroxy). In other effective compounds the electron-withdrawing groups are nitro, cyano, alkyl keto, or aryl keto and the electron-donating groups are amino or substituted amino, hydroxy, alkoxy, and phenoxy.

The pyrethroids photodecompose by a variety of processes, including ester cleavage, isomerization, and photooxidation of the *cis*-pentadienyl substituent of the pyrethrins, the furyl ring of resmethrin and kadethrin, and the isobutenyl methyl group and double bond of the chrysanthemates (Ruzo, 1982, 1983). The activity of dinitroanilines in photostabilizing such a variety of pyrethroids at 1:1 or 1:5 ratios probably results from competitive light absorption. However, the dinitroanilines are also effective at trace levels relative to the pyrethroids e.g., 1:10,000, suggesting that in these cases their action is not attributable to competition for light or a limiting reagent, e.g., oxygen or water. These photoquenchers have regions of high and low electron density and might complex with the excited state of the pyrethroid, possibly leading to energy dissipation by exciplex or charge-transfer quenching (Cowan and Drisko, 1976).

Pesticide interactions involve both photosensitization (e.g., rotenone enhances the photoisomerization of dieldrin; Ivie and Casida, 1970) and photostabilization (e.g., trifluralin retards the photooxidation of pyrethroids). Interactions of these types may be a disadvantage in inadvertently altering pesticide persistance or an advantage in possibly manipulating the effective life of pesticide resi-

dues. Appropriately substituted dinitroanilines may be useful photostabilizers under some conditions to prolong the residual persistence of photolabile pyrethroids and possibly other pesticides. This possibility remains to be tested under field conditions with toxicologically acceptable photostabilizers of adequate effectiveness.

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William Draper, Ella Kimmel, and other colleagues in the Pesticide Chemistry and Toxicology Laboratory provided valuable suggestions and assistance.

Registry No. 1, 1582-09-8; 2, 4726-14-1; 3, 19044-94-1; 4, 19044-88-3; 5, 33820-53-0; 6, 2077-99-8; 7, 445-66-9; 8, 317-70-4; 9, 393-77-1; pendimethalin, 40487-42-1; 4-nitrophenol, 100-02-7; 4-nitrocatechol, 3316-09-4; 4-nitroacetophenone, 100-19-6; 2-nitrophenetole, 610-67-3; nitrofen, 1836-75-5; 3-aminoacetophenone, 99-03-6; 3-hydroxyacetophenone, 121-71-1; 2,4-dihydroxyacetophenone, 89-84-9; phenothiazine, 92-84-2; 8-hydroxyquinoline, 148-24-3; azobenzene, 103-33-3; 2-nitrophenol, 88-75-5; chloromethoxynil, 32861-85-1; hydroxyquinone, 2474-72-8; chloranil, 118-75-2; acetophenone, 98-86-2; 2-hydroxybenzophenone, 117-99-7; diphenylamine, 122-39-4; triphenylamine, 603-34-9; 4-cyanophenol, 767-00-0; parathion, 56-38-2; piperonyl butoxide, 51-03-6; coumaphos, 56-72-4; carbazole, 86-74-8; benzimidazole, 51-17-2; tetramethrin, 7696-12-0; rotenone, 83-79-4; chlorobenzilate, 510-15-6; phenylthiourea, 103-85-5; (1*RS*)-*cis*-resmethrin, 10453-56-2; (1*RS*)-*trans*-tetramethrin, 5284-41-3; kadethrin, 58769-20-3; (1*R*,α*S*)-*cis*-cypermethrin, 65731-84-2; allethrin, 584-79-2.

Supplementary Material Available: One table listing 78 compounds with little or no effectiveness as photostabilizers for cyphenothrin on silica gel (1 page). Ordering information is given on any current masthead page.

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Synthesis and Some Larvicidal Properties of 2,3-Secopermethrin

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To examine structure–activity relationships of analogues closely related to permethrin, a synthetic chemical procedure for the preparation of *m*-phenoxybenzyl 5,5-dichloro-2-isopropyl-4-pentenoate (2,3-secopermethrin; **1**) has been developed. The reaction sequence included α-alkylation, ozonolysis, and introduction of the dichloromethylene group by the Wittig reaction. Side products from the Wittig reaction with bromotrichloromethane and triphenylphosphine were identified by mass spectrometry. Standardized laboratory bioassays with mosquito larvae (*Aedes aegypti L.*) indicated that (±)-**1** was about 50 times less active than a 46:54 cis–trans mixture of (±)-permethrin. The *m*-phenoxybenzyl ester of 5,5-dichloro-4-pentenoic acid was essentially inactive in the larvicidal tests.

Certain members of the new generation of synthetic pyrethroids, such as fenvalerate (Figure 1), do not possess a cyclopropane ring but have, instead, an isopropyl group adjacent to the ester linkage. This suggests that, with cyclopropyl pyrethroids such as permethrin, an insecticidally active analogue may be a ring-cleaved (seco) product. Of the three possible secopermethrins, 2,3-secopermethrin (**1**) is particularly intriguing because this structure, like fenvalerate, retains the α-isopropyl group. This compound has been described in the German patent literature (Winternitz, 1978; Mori and Omura, 1979), but comparisons of insecticidal properties to permethrin and fenvalerate have not been made. A variety of related acyclic esters have recently been synthesized and tested (Elliott et al., 1983).

This paper describes a small-scale preparation of **1** from 4-pentenoic acid and the evaluation of **1** in a mosquito bioassay screen. The larvicidal activity of this pyrethroid was compared to those of six racemic mixtures of permethrin and fenvalerate.

EXPERIMENTAL SECTION

Chromatography and Mass Spectrometry. Thin-layer chromatography was performed on precoated 5 × 20 cm silica gel 60 F-254 TLC plates (0.25-mm layer thickness, EM Laboratories) with visualization by UV light at 254

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