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.

ACKNOWLEDGMENT

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

Wesley G. Taylor* and Joseph A. Shemanchuk

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

Research Station, Agriculture Canada, Lethbridge, Alberta, Canada T1J 4B1.

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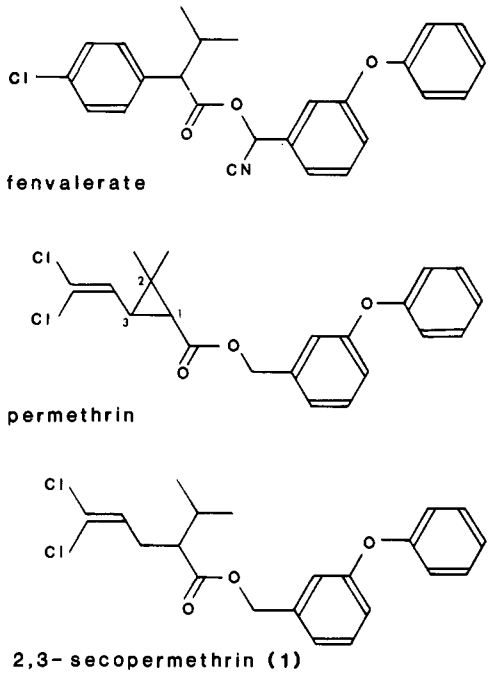


Figure 1. Chemical structures of synthetic pyrethroids referred to in this work.

nm. Gas chromatography was performed with a Hewlett-Packard Model 5838A gas chromatograph equipped with a flame ionization detector and a glass capillary column (22 m × 0.33 mm i.d.) coated with Carbowax 20M-TPA. A Hewlett-Packard 5985B combined gas chromatograph–mass spectrometer–data system equipped with a glass capillary column (25 m × 0.33 mm i.d.) of Carbowax 20M-TPA was employed for GC–MS analyses. Electron impact mass spectra (EI-MS) were recorded at 70 eV, whereas positive chemical ionization mass spectra (CI-MS) were recorded with isobutane as the reagent gas at a source pressure of 0.5 mmHg.

Syntheses. The following intermediates were prepared by procedures described in the literature: methyl 4-pentenoate (**2**) (Taylor, 1981); methyl 2-isopropyl-4-pentenoate (**3**) (Herrmann et al., 1973); methyl 2-isopropyl-4-oxobutanoate (**4**) (Taylor, 1979); (dichloromethylene)triphenylphosphorane (**5**) (Clement and Soulen, 1976); methyl 5,5-dichloro-2-isopropyl-4-pentenoate (**6**) (Taylor, 1981); 5,5-dichloro-2-isopropyl-4-pentenoic acid (**7**) (Taylor, 1981). With the exception of **5**, these compounds were characterized by proton nuclear magnetic resonance (Varian Model EM 360A NMR) and infrared (Perkin-Elmer Model 137 IR) spectroscopy and by mass spectrometry. **6a–c** were characterized by mass spectrometry. The synthetic details, purification methods, and spectra of these compounds are provided as supplementary material (see paragraph at the end of the paper regarding supplementary material).

***m*-Phenoxybenzyl 5,5-dichloro-2-isopropyl-4-pentenoate (1)** was prepared from **7** (0.633 g, 3 mmol), thionyl chloride (0.86 g, 7.3 mmol), and *m*-phenoxybenzyl alcohol (0.63 g, 3.15 mmol) according to the procedure of Nakatsuka et al. (1977). After column chromatography (silicAR cc-7) with hexane–ether mixtures, **1** was isolated (0.658 g, 56% yield) as a colorless oil: bp 174–176 °C (0.1 mmHg); TLC R_f = 0.4 (hexane–ether, 10:1); IR (neat) 1575, 1625, and 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.57–6.80 (9 H, m), 5.82 (1 H, m), 5.12 (2 H, s), 2.63–1.47 (4 H, m), 0.98 (3 H, s), 0.88 (3 H, s); EI-MS m/z (rel intensity) 392 (M^+· for Cl = 35, 3.2), 200 (3), 184 (16), 183 (100); CI-MS m/z (rel intensity) 393 (MH^+ for Cl = 35, 65), 357 (48), 321 (13), 213 (11), 210 (15), 185 (57), 184 (21), 183 (100). Anal. Calcd for $C_{21}H_{22}Cl_2O_3$: C, 64.13; H, 5.64; Cl, 18.03. Found: C, 64.26; H, 5.76; Cl, 18.30.

***m*-Phenoxybenzyl 5,5-dichloro-4-pentenoate (8)** was prepared from 5,5-dichloro-4-pentenoic acid (2.2 g, 13 mmol) (Taylor, 1981) as described for the preparation of **1**. After column chromatography, 1.536 g (40% yield) of **8** was obtained, as a faint yellow oil: bp 173–174 °C (0.1 mmHg); TLC R_f = 0.3 (hexane–ether, 10:1); IR (neat) 1580, 1620, and 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.57–6.73 (9 H, m), 5.85 (1 H, m), 5.08 (2 H, s), 2.67–2.23 (4H, m); EI-MS m/z (rel intensity) 350 (M^+· for Cl = 35, 6), 200 (3), 184 (14), 183 (100); CI-MS m/z (rel intensity) 351 (MH^+ for Cl = 35, 7), 315 (13), 225 (6), 186 (7), 185 (46), 184 (22), 183 (100). Anal. Calcd for $C_{18}H_{16}Cl_2O_3$: C, 61.55; H, 4.59; Cl, 20.19. Found: C, 61.78; H, 4.30; Cl, 19.92.

Source of Other Pyrethroids. Technical-grade permethrin, obtained from ICI Americas, Inc., Goldsboro, NC, and labeled as 40.83% *cis*- and 53.10% *trans*-permethrin, was purified by dry column chromatography (Loev and Goodman, 1967). Initially, a 10-g sample was purified without isomer separation in nylon tubing (68 × 3 cm) containing the adsorbent (Woelm TSC silica gel and fluorescent indicator, ICN Nutritional Biochemicals, Cleveland, OH) and with a solvent mixture of hexane–ether–methanol, 10:5:1. A main band at 38–50 cm from the origin was removed and washed with EtOAc. The resulting oil (8.7 g) contained 45.9% *cis*- and 54.1% *trans*-permethrin by integration of peak areas from GC. These isomers were also detected by TLC with petroleum ether–methanol (95:5; R_f = 0.65 and 0.70), hexane–ether (10:1; R_f = 0.4 and 0.5), hexane–methanol (99:1; R_f = 0.3 and 0.5), and hexane–EtOAc (10:1; R_f = 0.4 and 0.5).

With the same dry column procedure, 8 g of technical permethrin was separated with petrolum ether–methanol, 20:1, into three bands, at 17–27, 13–17, and 9–13 cm from the origin. The sample from the 17–27-cm band was isolated (2.8 g) and recrystallized from hexane to give predominantly *cis*-permethrin (2.5% trans isomer by GC), as a white solid. The sample obtained from the 9–13-cm band (2.0 g) was rechromatographed on a dry column (62 × 2 cm) with the above solvent system. The 10–18-cm band from this column gave a sample of *trans*-permethrin (3.8% cis isomer by GC), as a faint yellow oil.

Samples of fenvalerate were used as received from Shell Canada, Ltd., Oakville, Ontario, Canada, either as the technical-grade material (92.4% active ingredient) or as analytical standards of the *SS/RR* and *RS/SR* enantiomeric pairs.

Mosquito Bioassays. Insecticidal toxicity was determined with late third instar larvae from a laboratory colony of *Aedes aegypti* (L.) mosquitoes. The bioassay technique was similar to the procedure described by the World Health Organization (1963). Temperature of the test room was 20 ± 1 °C. Glass beakers (400 mL) were used, each containing 250 mL of distilled water and 25 larvae. Tests were run in triplicate, with five concentrations per test. Chemical solutions (freshly prepared) were made up in 95% ethanol so that 1 mL of solution was added to each beaker. Beakers containing the control larvae received 1 mL of solvent, giving a range of mortality from 0 to 6%. The dilution factor within a series of concentrations was usually linear (e.g., 5-, 10-, 15-, 20-, and 25-ppb final concentration). Mortality of larvae was counted after 24 h, the criterion for mortality being the inability of the larvae to surface. LC_{50} and LC_{90} values and the slope of the regression line were obtained by probit analysis (Finney, 1964) using an IBM 370 computer. All bioassays were

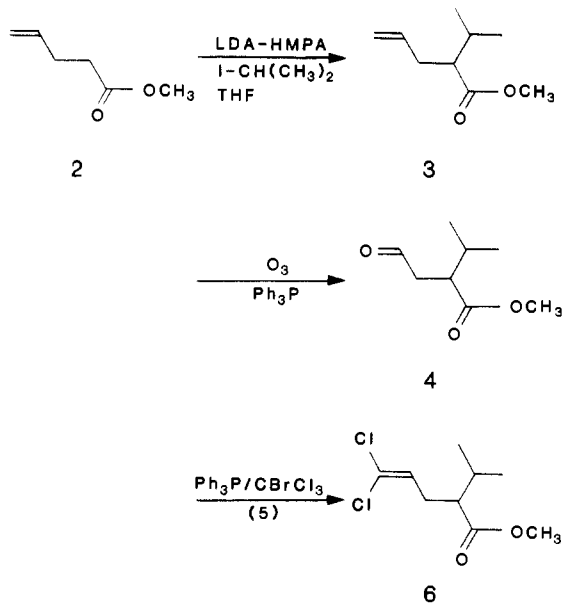


Figure 2. Synthesis of methyl 5,5-dichloro-2-isopropyl-4-pentenoate.

repeated at least 5 times, using new test solutions and larvae from different batches of eggs. The mean values of the data are reported.

RESULTS AND DISCUSSION

Preparation of Intermediates. With a 1:1 complex of lithium diisopropylamide (LDA) and hexamethylphosphoramide (HMPA) as a nonnucleophilic base, the enolate anion of **2** was formed in tetrahydrofuran solution and was allowed to react at −78 °C with a slight excess of 2-iodopropane. Under these conditions (Figure 2), **3** was obtained in yields ranging from 85 to 90%. Without the use of HMPA (Cregge et al., 1973), approximately an equal mixture of **2** and **3** was isolated.

The terminal olefinic group in **3** was allowed to react in CH_2Cl_2 solution with ozone at −78 °C. Following workup with excess triphenylphosphine as the reducing agent, the ester aldehyde (**4**) was isolated. The identity of **4** was suggested from its spectral properties and from the properties of its crystalline 2,4-dinitrophenylhydrazone derivative. This aldehyde was used without purification in the next step.

Introduction of the dichloromethylene group was accomplished by use of **5**, a ylide that has been prepared to advantage by the interaction of bromotrichloromethane with triphenylphosphine (Clement and Soulen, 1976) rather than by an older method with carbon tetrachloride and triphenylphosphine. We recently demonstrated that **5**, initially developed for the conversion of acyl cyanides to 2-substituted 3,3-dichloroacrylonitriles, was useful for the preparation of 1,1-dichloroolefins from some aliphatic aldehydes (Taylor, 1981). The nitrogenous phosphorus ylide, (dichloromethylene)tris(dimethylamino)-phosphorane), has also been used for the preparation of 1,1-dichloroolefins from aldehydes (Salmond, 1977; Taylor, 1980) but was not utilized in the present work.

To generate **5** for introduction of the dichlorovinyl group with the Wittig reaction, an excess of bromotrichloromethane and triphenylphosphine was allowed to react in benzene at 5 °C (eq 1). The isopropyl ester aldehyde (**4**)

$$2Ph_3P + CBrCl_3 \longrightarrow \underset{5}{Ph_3P{=}CCl_2} + \underset{5b}{Ph_3PBrCl} \qquad (1)$$

was then added and the reaction was continued by stirring at room temperature. Capillary GC and GC–MS analysis

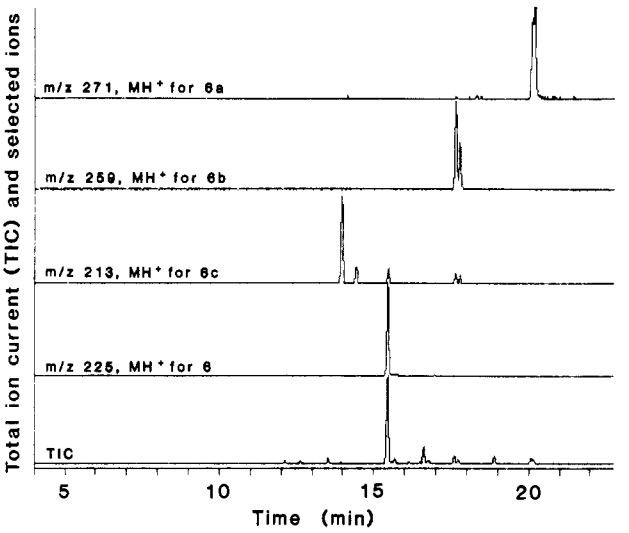
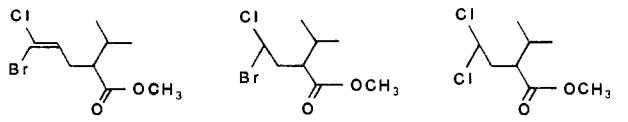


Figure 3. Ion chromatograms from the CI-MS analysis of a crude Wittig reaction product. One microgram of the mixture was injected split, with GC column temperature programming from 60 °C at 3 °C/min.



6a 6b 6c

Figure 4. Proposed chemical structures of side products from the Wittig reaction with bromotrichloromethane and triphenylphosphine.

on the hexane-soluble product indicated that one main component was present. The identity of **6** in purified samples was verified by interpretation of the EI-MS and CI-MS and from the IR and ^1H NMR spectra.

GC–MS of Halogenated Side Products. The total ion mass chromatograms from crude samples of dichlorovinyl ester (**6**) indicated that several minor side products were formed during the Wittig reaction with bromotrichloromethane and triphenylphosphine. It was of interest to identify these components, and the products from this reaction were analyzed in some detail. There was a possibility that methyl 5-bromo-5-chloro-2-isopropyl-4-pentenoate (**6a**) would be formed if (bromochloromethylene)triphenylphosphorane (**5a**) was generated (eq 2) and was capable of competing with **5** for the aldehyde

$$2Ph_3P + CBrCl_3 \longrightarrow \underset{5a}{Ph_3P{=}CBrCl} + \underset{5c}{Ph_3PCl_2} \qquad (2)$$

component. The dihalides **5b** (eq 1) and **5c** (eq 2) must also be generated in order to satisfy the stoichiometry of ylide formation. Dichloride (**5c**), already known to be capable of reacting with aldehydes, has limited the synthetic utility of Wittig reactions with carbon tetrachloride and triphenylphosphine. Using CI-MS, a search was made for these three side products by searching for their expected quasi-molecular ions in the mass chromatogram obtained on the crude product from the Wittig reaction (Figure 3). These selected ion tracings provided evidence that the expected bromochloro olefin (**6a**), methyl 4-bromo-4-chloro-2-isopropylbutanoate (**6b**), and methyl 4,4-dichloro-2-isopropylbutanoate (**6c**) were formed (Figure 4). Further evidence for their identity was obtained by interpretation of their EI-MS.

The peak for bromochloro olefin (**6a**) at 20.1–20.2 min (Figure 3) was quite broad under these GC–MS conditions.

Table I. Toxicities of Synthetic Pyrethroids to Late Third Instar Larvae (*A. aegypti*)

pyrethroid	isomeric purity, %	lethal conc, ppb LC_{50}	LC_{90}	slope
permethrin	*a*	0.24	0.52	3.74
(1*RS*)-*trans*-permethrin	96.2	0.25	0.49	4.43
(1*RS*)-*cis*-permethrin	97.5	0.26	0.65	3.39
fenvalerate	*b*	0.47	1.22	3.24
(*SS*/*RR*)-fenvalerate	99.9	0.28	0.78	2.95
(*RS*/*SR*)-fenvalerate	97.0	5.09	16.45	2.51
2,3-secopermethrin (1)	*c*	12.35	22.50	5.05
desisopropyl ester (8)		>5000[d]		

[a] A 45.9:54.1 mixture of (±)-cis and (±)-trans isomers. [b] Approximately an equal mixture of four isomers. [c] Approximately an equal mixture of two isomers. [d] 24% mortality at 5.12 ppm.

By optimization of the chromatographic conditions, two distinct peaks (1:1 peak area ratio) were seen, and each gave nearly identical mass spectra. These components probably represented geometrical isomers of **6a**, of the *E* and *Z* type. The two peaks near 17.6 and 17.7 min also gave identical mass spectra and probably represented diastereomeric mixtures of **6b**, because two asymmetric centers (at C-2 and C-4) are present. The peak for **6c** occurred at 14.0 min. The three side products accounted for approximately 18% of the crude reaction mixture, 7% for **6a**, 8% for **6b**, and 3% for **6c**. No attempt was made to isolate these side products.

Basic hydrolysis of **6** (~95% pure after column chromatography) gave dichlorovinyl acid **7**, which was converted to **1** by standard procedures.

Testing Results. Samples of permethrin, 1*RS*-*trans*-permethrin, and 1*RS*-*cis*-permethrin were nearly equipotent as mosquito larvicides and gave LC_{50}–LC_{90} values in the range of 0.24–0.65 ppb (Table I). Although the insecticidal activity is primarily associated with the 1*R* enantiomers of this synthetic pyrethroid, racemic mixtures of similar isomeric content also showed small differences in potency during bioassays with houseflies and mustard beetles (Burt et al., 1974). Other investigators have shown that permethrin, usually tested as a nearly equal mixture of 1*RS*-cis and 1*RS*-trans isomers, was active against various species of mosquito larvae in the ppb range (Mulla et al., 1975; Mulla and Darwazeh, 1976; Rettich, 1979; Mulla et al., 1980; Herald et al., 1980).

A technical mixture of fenvalerate was also tested, along with two pairs of its enantiomers (Table I). The most active enantiomeric pair was *SS*/*RR*, which was about 18-fold more potent than the *RS*/*SR* enantiomers. Elliott et al. (1978) have shown that the most insecticidally active enantiomer of this pyrethroid (against houseflies and mustard beetles) has the *S* configuration in the acid and alcohol moieties.

When the larvicidal properties were compared to permethrin, the data showed that fenvalerate, which exists as a mixture of *SS*/*RR* and *RS*/*SR* isomers, was approximately half as potent, whereas **1**, which exists as a mixture of an *R* and *S* enantiomer, was about one-fiftieth as potent. Although cleavage of the 2,3-position in permethrin is detrimental to activity, the activity was not abolished as was the case for the monosubstituted ester (**8**). This study reinforces the idea (Elliott et al., 1983) that two α-substituents are important structural features for insecticidal activity in acyclic analogues of pyrethroid acids.

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Registry No. (±)-**1**, 88496-52-0; **2**, 818-57-5; (±)-**3**, 88496-53-1; (±)-**4**, 88496-54-2; (±)-**4** 2,4-dinitrophenylhydrazone, 88496-55-3; (±)-**6**, 88496-56-4; (±)-(*Z*)-**6a**, 88496-57-5; (±)-(*E*)-**6a**, 88496-62-2; (±)-**6b** (isomer I), 88496-58-6; (±)-**6b** (isomer II), 88496-63-3; (±)-**6c**, 88496-59-7; diisopropylamine, 108-18-9; 5,5-dichloro-2-isopropyl-4-pentenoic acid, 88496-60-0; *m*-phenoxybenzyl 5,5-dichloro-2-isopropyl-4-pentenoate, 88496-61-1; (1*RS*)-*trans*-permethrin, 52341-32-9; (1*RS*)-*cis*-permethrin, 52341-33-0; (*SS*/*RR*)-fenvalerate, 67890-40-8; (*RS*/*SR*)-fenvalerate, 67890-39-5.

Supplementary Material Available: Synthetic procedures and IR, ^1H NMR, and mass spectral data supplemental to those in the text (4 pages). Ordering information is given on any current masthead page.

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