Studies on Synthetic Pyrethroids 6-Synthesis of 2-(3-phenoxybenzoyl) 2-propyl esters for Deltamethrin and Fenpropathrin

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ABSTRACT

The benzilic position of Deltamethrin and Fenpropathrin reacts readily with acetone to give 2-(3-phenoxybenzoyl)-2-propyl ester in crystalline form. The melting point values are 90-91°C and 86-87°C for the acetonic derivatives of Deltamethrin and Fenpropathrin, respectively. The yield products of acetone derivative for deltamethrin and Fenpropathrin are 94.3% and 97%, respectively. The spectrometry, using n.m.r. and i.r. techniques, was applied to confirm the structure of the acetone derivatives. The n.m.r. spectra for both derivatives show the loss of CHCN group at 6.32 ppm and an addition of two methyl groups from acetone at 0.75 and 1.58 ppm. The i.r. spectra establishes the presence of both ester and ketone carbonyl bands at 1720 and 1685 cm^{-1} for both products.

INTRODUCTION

Significant changes in the types of insecticides in the past two decades has been achieved in that several insecticides have been banned or are being used under certain restrictions. Synthetic pyrethroids are coming to replace these compounds, especially those having properties of selectivity and safety. The major commerical and experimental pyrethroid insecticides are esters of 3- phenoxybenzyl alcohol or α-cyano-3-phenoxybenzyl alcohol.

The preparation of 3-phenoxybenzyl chrysanthemates and their dihalovinyl analogs substituted with cyanogroup was described by several authors, e.g. Katsuda[1] and 2. Kondo[3], Elliot[4], Lantzch[5], Omura[6], Kurary[7]. Other chrsanthemate pyrethroids were also prepared and tested as insecticides by Aratani[8] and Kondo[9].

Since α-cyanophenoxybenzyl pyrethroids are ready to react at the position of α-cyano[10,11], the aim of the present study is to synthesize 2-(3-phenoxybenzoyl)-2-propyl esters of Deltamethrin and Fenpropathrin to be examined as insecticides.

MATERIALS AND METHODS

Pesticides Used

The following compounds were used:

A. Deltamethrin (decamethrin, Decis, NRDC 161): α-cyano-3-phenoxybenzyl cis-3-(2,2-dibromovinyl)2,2-dimethylcyclopropane carboxylate, a technical grade (>98% a.i.) was used as a single isomer.

B. Fenpropathrin (meothrin, 5-3206): α-cyano-3-phenoxybenzyl-2,2,3,3-tetramethylcyclopropane carboxylate, pure material (≅100% a.i.) was used.

Table 1 indicates that percent yield for derivatives are higher than 90%. However, the yield of isolated derivatives for Deltamethrin and Fenpropathrin were 94.3 and 97%, respectively. The reaction was carried out by Saleh[10] and Marei[11] to achieve derivatives more sensitive for e.c.d. glc. The reaction was repeated in this investigation to check the biological effects of these derivatives as insecticides.

B. Confirmatory Tests

1. Nuclear Magnetic Resonance (^{1}H n.m.r.)

In order to confirm the structure of chemical products, the nuclear magnetic resonance was run using a Varian EM-390 spectrometer with tetramethyl silane (TMS) as an internal standard and deutero chloroform as a solvent. The obtained results for n.m.r. spectra are in agreement with results of Saleh[10] and Table 2 compares the results of the present work and those obtained by him for Deltamethrin derivative. The present study for the preparation of fenpropathrin-acetone derivative showed the same results. However, n.m.r. established that the CHCN proton is lost and two additional methyl groups are introduced (Fig. 2 and 3). Thus the product is an ester derived by loss of the elements of hydrogen cyanide and an addition of those of acetone to the alcohol moiety.

2. Infrared (I.R.) Spectroscopy

The results are similar to those achieved by Saleh[10]. The data presented in Table 2 indicate these findings for Deltamethrin derivative. The present study for the preparation of Fenpropathrin-acetone derivative showed the same results. Fig. 4 and 5 established the presence of both ester and ketone carbonyl bands at 1720 and 1685 cm^{-1}, respectively.

3. Melting Point

The melting point for each crystalline form, i.e. Deltamethrin and Fenpropathrin and their derivatives, was obtained using an electro-thermal melting point apparatus (Gallenkamp, England). The results in Table 1 show that the values of the melting point of 2-(3-phenoxybenzoyl)-2-propyl-2,2-dimethyl-3-(2,2-dibromovinyl)-cyclopropanecarboxylate (Deltamethrin-acetone derivative) and 2-(3-phenoxybenzoyl)-2-propyl-2,2,3,3-tetramethyl-cyclo propanecarboxylate are 90-91°C and 86-87°C, respectively, which are different from those obtained for α-cyano-3-phenoxybenzyl-cis-3-(2,2-dibromovinyl)-2-2-dimethylcyclo propanecarboxylate (Deltamethrin) and α-cyano-3-phenoxybenzyl-2,2,3,3-tetramethylcyclopropanecarboxylate (Fenpropathrin).

The combined results of these tests lead to the conclusion that the products of the present reaction are 2-(3-phenoxybenzyol)-2-propyl esters.

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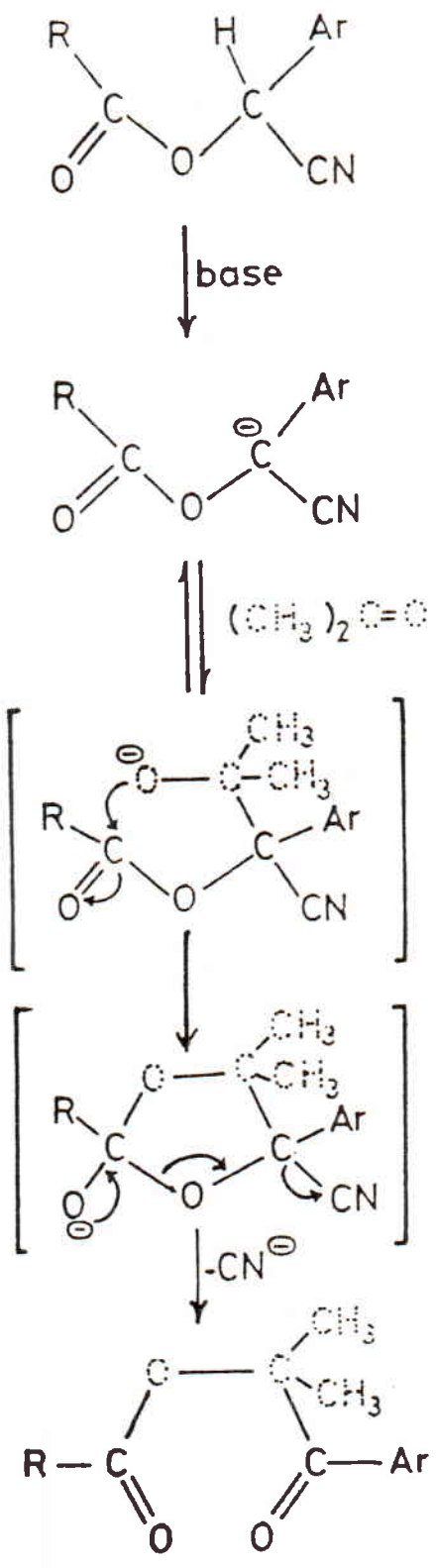

Figure 1 : Derivatization of ∝-cyanophenoxybenzyl pyrethroids at the benzilic position. R is a portion of the acid moiety of the pyrethroid and 'Ar' is 3-phenoxyphenyl or phenyl. (Saleh, Marei and Casida 1980).

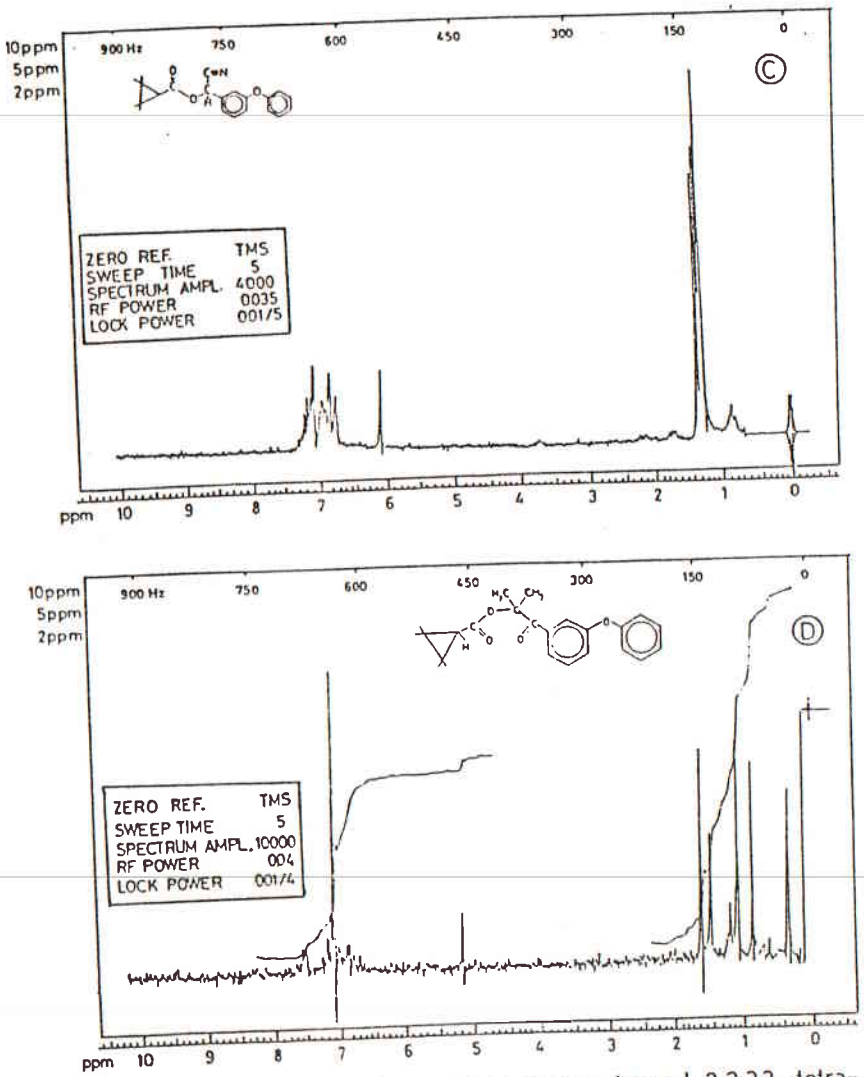

Figure 3 : N.M.R. spectra of ∝-cyano-3-phenoxybenzyl-2,2,3,3-tetramethyl cyclopropanecarboxylate, fenpropathrin, (C) and 2-(3-phenoxybenzoyl)-2-propyl-2,2,3,3-tetramethyl-cyclopropanecarboxylate, fenpropathrin-acetone derivative, (D).

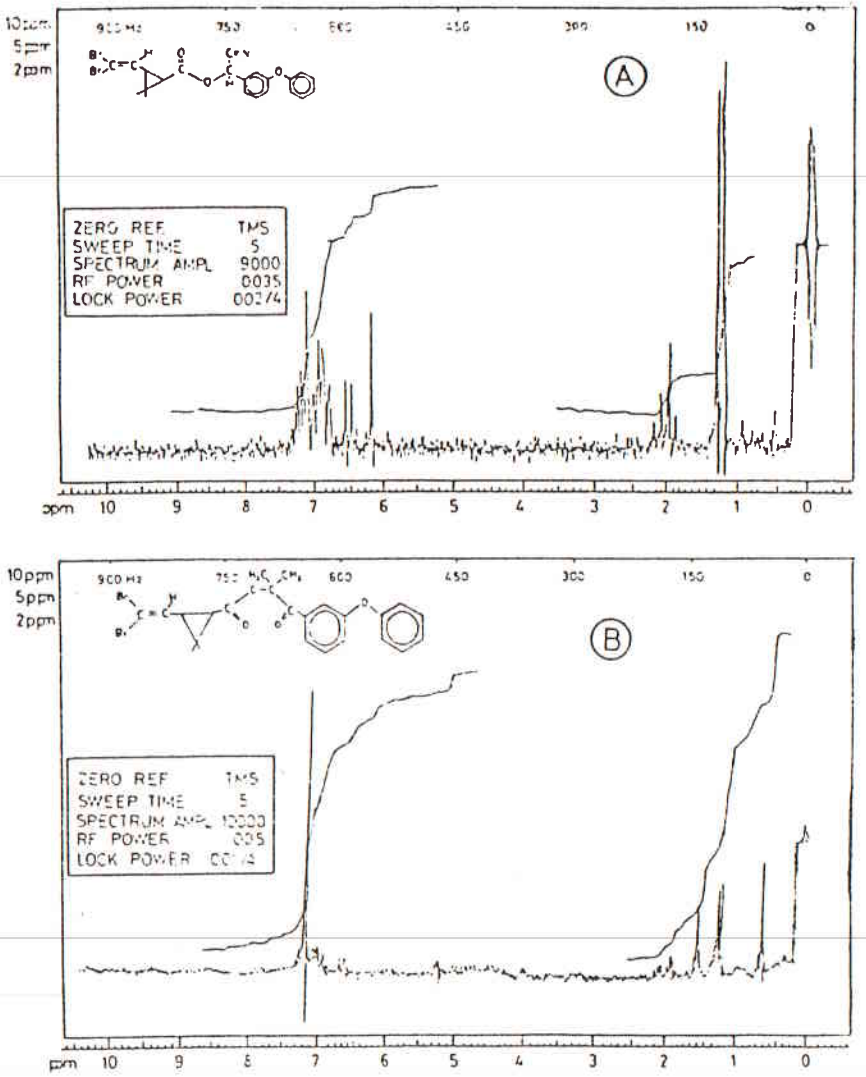

Figure 2 : N.M.R spectra of ∝-cyano-3-phenoxybenzyl-2,2-dimethyl-3-(2,2-dibromovinyl)-cyclopropanecarboxylate, deltamethrin, (A) and 2-(3-phenoxybenzoyl)-2-propyl-2,2-dimethyl-3-(2,2-dibromovinyl)-cyclopropanecarboxylate, deltamethrin-acetone derivative, (B).

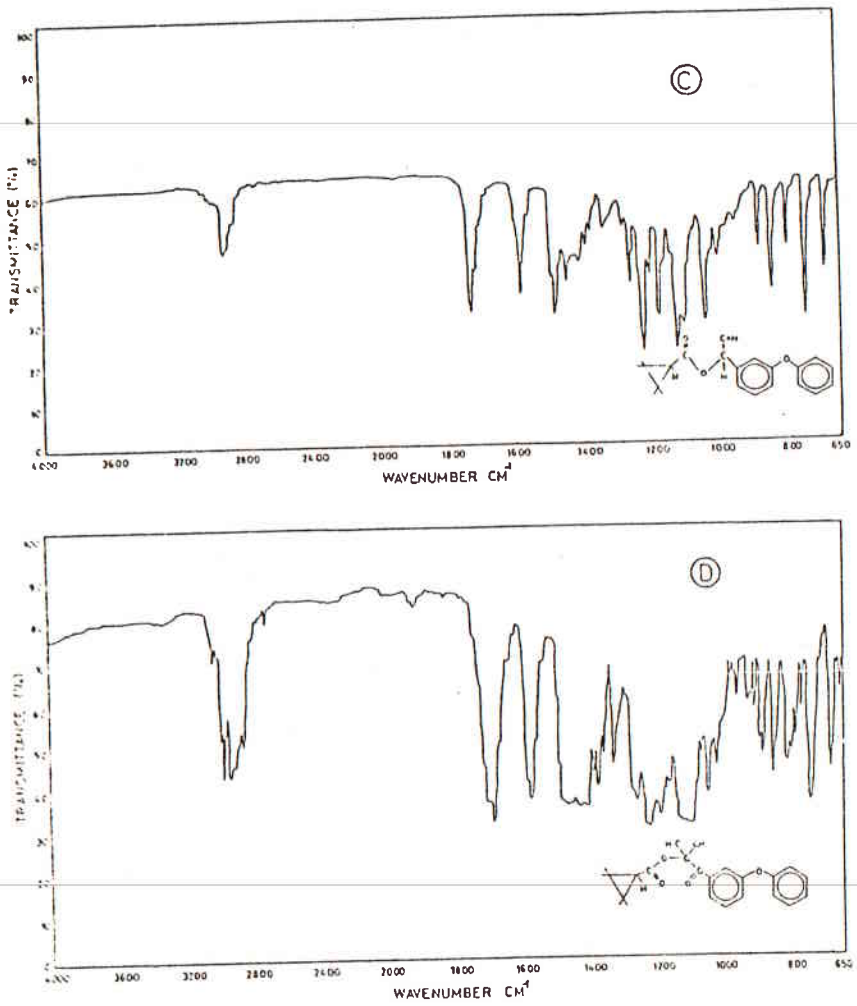

Figure 5: I.R. spectra of ∝-cyano-3-phenoxybenzyl-2,2,3,3-tetramethyl cyclopropanecarboxylate, fenpropathrin, (C) and 2-(3-phenoxybenzoyl)-2-propyl-2,2,3,3-tetramethyl-cyclopropanecarboxylate, fenpropathrin-acelone derivative, (D).

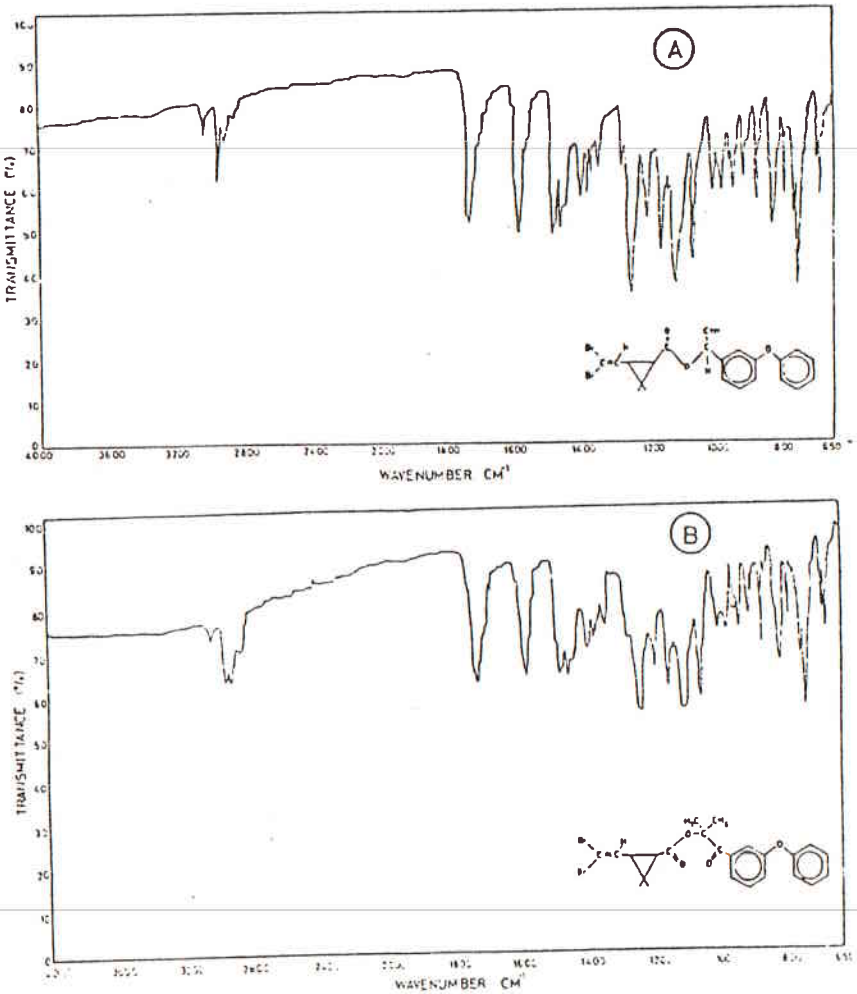

Figure 4 : I.R. spectra of ∝-cyano-3-phenoxybenzyl-2,2-dimethyl-3-(2,2-dibromovinyl)-cyclopropanecarboxylate, deltamethrin, (A) and 2-(3-phenoxybenzoyl)-2-propyl-2,2-dimethyl-3-(2,2-dibromovinyl)-cyclopropanecarboxylate, deltamethrin-acelone derivctive (B).

Table 2: Nuclear magnetic resonance (NMR) Shifts (δ) of methyl groups and benzilic substituents and Infrared (IR) presence of both ester and ketone carbonyl bands.

Substituents or bands	NMR				IR			
	deltamethrin		deltamethrin acetone derivative		deltamethrin		deltamethrin acetone derivative	
	present work	Saleh et al (1980)	present work	Saleh et al, (1980)	present work	Saleh et al (1980)	present work	Saleh et al, (1980)
CH_3	1.31, 1.21	1.27, 1.19	1.58, 1.35 1.25, 0.75	1.67, 1.66 1.21, 0.87	-	-	-	-
CHCN	6.32	6.32	-	-	-	-	-	-
Ester bond	-	-	-	-	-	-	$1720Cm^{-1}$	$1720Cm^{-1}$
Ketone bond	-	-	-	-	-	-	$1685Cm^{-1}$	$1685Cm^{-1}$

R E F E R E N C E S

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