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Facile One-Pot Synthesis of an Insecticide Intermediate

Wynona M. P. Johnson and George Holan

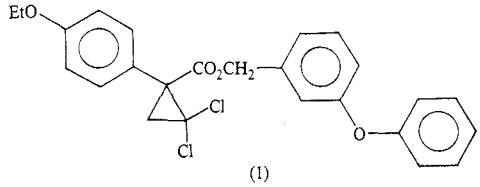
Division of Applied Organic Chemistry, CSIRO,
P.O. Box 4331, Melbourne, Vic. 3001.

Abstract

A new insecticide, 3-phenoxybenzyl 2,2-dichloro-1-(2,2-dichlorovinyl)cyclopropane-1-carboxylate (7), has been synthesized in two steps from a readily available acrylate (2). The first step conveniently accomplished four distinct chemical transformations in one pot.

Introduction

Recently we reported a new group of insecticides.[1] These compounds have combined pyrethroid–DDT structures, e.g. (1). In connection with this research program we wished to synthesize analogues of these insecticides, where the aryl group on the cyclopropane ring was replaced by a pyrethroid side chain. We now report the synthesis, in 69% overall yield, of a new insecticide (7). The required skeleton is prepared by a facile one-pot procedure, which is then followed by an esterification reaction. The biological results will be reported elsewhere.



(1)

Results and Discussion

Initially we carried out the synthesis of compound (7) in a stepwise manner (see Scheme 1), isolating compounds (3)–(7) individually for characterization. Since all the reactions for transformations *a* → *d* required NaOH as a reagent and used either $CHCl_3$ or MeOH as solvent, we felt that by judicious choice of conditions a simple one-pot synthesis might be possible.

Makosza and Fedorynski[2] reported the nucleophilic displacement of a cyano group from a thiocyanate by the trichloromethyl anion (generated from 50% aqueous

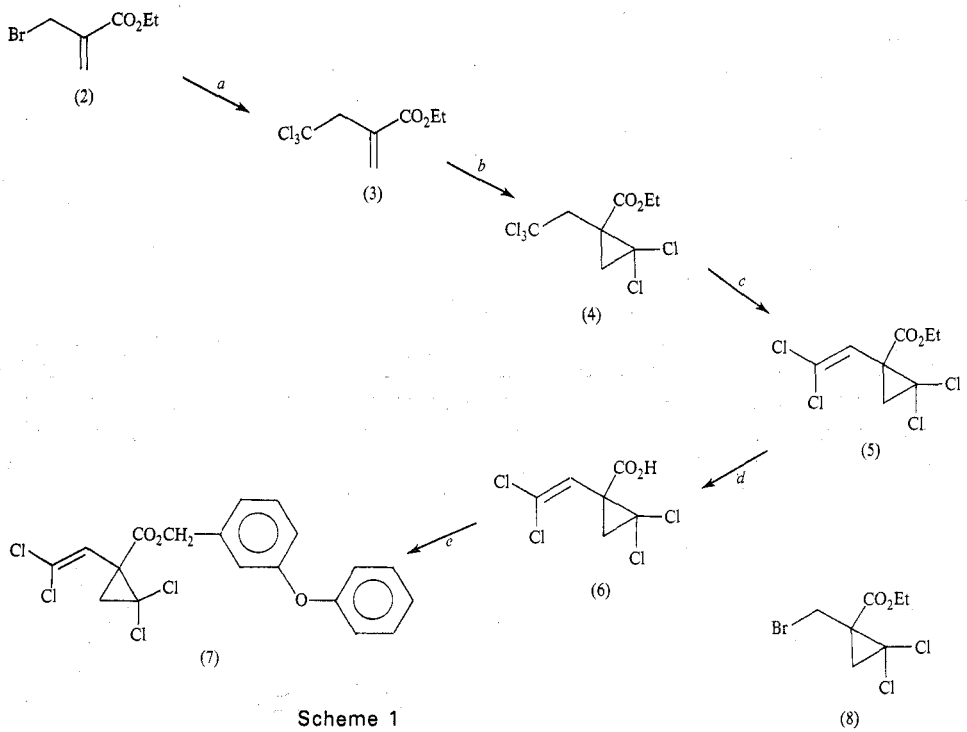
[1] Holan, G., O'Keefe, D. F., Virgona, C., and Walser, R., *Nature* (*London*), 1978, **272**, 734.
[2] Makosza, M., and Fedorynski, M., *Synthesis*, 1974, 274.

NaOH, $CHCl_3$ and benzyltriethylammonium chloride). However, Baird and Baxter[3] reported that their attempts to displace an allylic bromo group under the above reaction conditions were not successful. We found that this displacement was a significant pathway only at temperatures below 4° and when NaCl was added. Presumably the CCl_3^- anion is not sufficiently stable at higher temperatures, and the added NaCl would keep the equilibrium

$$^-CCl_3 \rightleftharpoons :CCl_2 + Cl^-$$

over to the left, preventing the dissociation of the CCl_3^- anion.

By contrast, above 4° the dichlorocarbene added to the bromo acrylate (2) to generate compound (8). This was not converted into the trichloromethyl compound (4) under any of the conditions attempted.



Scheme 1

For the next stage of the one-pot reaction, after all of the allylic bromo group had been replaced by the CCl_3 group, the temperature was allowed to rise to 20° and the dichlorocarbene addition to the double bond then took place. We hoped that addition of dilute NaOH to the reaction mixture containing compound (4) would facilitate dehydrohalogenation, *c*, and hydrolysis, *d*. However, under these conditions only the hydrolysis was achieved and not the dehydrohalogenation.

Replacement of the chloroform by 5% NaOH/methanol smoothly accomplished both transformations *c* and *d*. The overall yield of (2) → (6) was 70%. Esterification of the acid (6) with 3-phenoxybenzyl alcohol gave the desired insecticide, 3-phenoxybenzyl 2,2-dichloro-1-(2,2-dichlorovinyl)cyclopropane-1-carboxylate (7).

[3] Baird, M. S., and Baxter, A. G. W., *J. Chem. Soc., Chem. Commun.*, 1979, 210.

Experimental

Microanalyses were carried out by the Australian Microanalytical Service, Melbourne. Melting points were determined on a Mettler FP52 hot-stage apparatus and are uncorrected. Proton magnetic resonance spectra were recorded at 60 MHz with Varian Associates T60 or EM360 spectrometers, with tetramethylsilane as an internal standard and (D)chloroform as solvent. Infrared spectra were recorded on a Perkin–Elmer 710B spectrometer. Merck silica gel (60–230 mesh) was used for chromatography.

Preparation of 2,2-Dichloro-1-(2,2-dichlorovinyl)cyclopropane-1-carboxylic Acid (6)

To an ice-cold solution of ethyl α-(bromomethyl)acrylate (2)[4] (1 g, 5 mmol), sodium chloride (500 mg) and benzyltriethylammonium chloride (90 mg, 0·375 mmol) in chloroform (10 ml), under an inert atmosphere, was added aqueous sodium hydroxide (10 ml, 50% w/w). The reaction was stirred at 0–4°, for 24 h, followed by 1 h at room temperature. The chloroform was then removed under vacuum and 5% NaOH/MeOH (24 ml) added. The resulting suspension was stirred at room temperature for 3 h. The methanol was then removed under vacuum. Water (100 ml) was added and the slurry filtered. The aqueous filtrate was acidified and thoroughly extracted with ether. This ether extract was washed with water and saturated NaCl solution and dried over anhydrous $MgSO_4$. The concentrated residue was recrystallized from light petroleum (60–80°) to afford the desired *product* (6) (910 mg, 70%), m.p. 105–107° (Found: C, 28·7; H, 1·7; Cl, 56·4. $C_6H_4Cl_4O_2$ requires C, 28·8; H, 1·6; Cl, 56·7%). ^{1}H n.m.r. δ 1·9, 2·65, 2H, AB system, J 9 Hz; 6·3, 1H, s, CH=; 10·4, 1H, s, CO_2H. Infrared ν_{max} (Nujol) 1710, 1620 cm^{-1}.

Preparation of Ester (7)

To a solution of carboxylic acid (6) (0·25 g, 1 mmol) in anhydrous tetrahydrofuran (1·5 ml) was added 1,1-carbonyldiimidazole (0·18 g, 1 mmol) and stirring continued for 1 h. At the end of this time, a solution of 3-phenoxybenzyl alcohol (0·21 g, 1 mmol) and sodium (1·5 mg) in anhydrous tetrahydrofuran (1·5 ml) was added, and stirring was continued for 2 h. Then water and ether were added, and the layers separated. The ether layer was washed successively with saturated $NaHCO_3$ solution, water, saturated NaCl solution, and dried over anhydrous $MgSO_4$. The concentrated extract was purified by chromatography on silica gel with 1 : 1 light petroleum (60–80°)/chloroform as the eluting solvent to afford the 3-phenoxybenzyl ester (7) as a viscous *oil* (0·43 g, 99%) (Found: C, 52·5; H, 3·4; Cl, 33·0. $C_{19}H_{14}Cl_4O_3$ requires C, 52·8; H, 3·3; Cl, 32·8%). ν_{max} (film) 1738, 1610, 1590 cm^{-1}. N.m.r. δ 1·84, 2·63, 2H, AB system, J 9 Hz; 5·17, 2H, s, CH_2Ar; 6·33, 1H, s, CH=; 6·87–7·47, 9H, m, aromatics.

Acknowledgment

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[4] Ferris, A. F., *J. Org. Chem.*, 1955, **20**, 780.