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SYNTHESIS OF 2-ALKYLTHIO (OR TRIFLUOROMETHYLTHIO)-2-HALOGENO-ETHENYL DERIVATIVES BY MEANS OF WITTIG (UNDER PHASE TRANSFER CONDITIONS) OR WITTIG-HORNER REACTIONS. APPLICATION IN THE FIELD OF PYRETHROIDS.

REMO GALLI*, LEONARDO SCAGLIONI
Laboratorio di Chimica Organica, Istituto di Biochimica Generale, Facoltà di Agraria, Via Celoria,2, I-20133 Milano, Italy

and

OTTORINO PALLA, FRANCO GOZZO
Centro Ricerche Antiparassitari, Farmoplant, Via Bonfadini, 148, I-20138 Milano, Italy.

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Abstract. A mixture of $RSCHCl_2$, Ph_3P and trans-caronaldehyde ethyl ester, treated with aq.NaOH under phase transfer conditions, gave the corresponding 2-alkylthio,2-chloroethenyl derivative, the product of the Wittig reaction of a phosphorane formed 'in situ'. The analogous derivative of the cis- and the 2-methylthio, 2-bromoethenyl derivative of the trans-caronaldehyde ethyl ester were synthesized also by means of Wittig-Horner reactions. The 2-trifluoromethylthio, 2-chloroethenyl derivative of the caronaldehyde ethyl ester (cis-trans mixture) was also obtained through the phosphonate prepared from

$$CF_3SCl + N_2CHP(O)(OEt)_2 \longrightarrow CF_3SCHClP(O)(OEt)_2$$

The new derivatives prepared were converted to final pyrethroids by esterification with cyano(m-phenoxyphenyl)methanol.

Synthetic pyrethroids are well known compounds derived from modification of the insecticidal esters found in natural pyrethrum[1]. The modifications operated on the natural structures led to the synthesis of compounds in which high activity against insects and low mammalian toxicity are combined with increased photostability, so that they are suitable for agricultural uses. Apart from structures like Fenvalerate[2], which are esters of α-alkyl-phenylacetic acids, the pyrethroids are esters of 3-(2,2-substituted-ethenyl)-2,2-dimethyl-cyclopropanecarboxylic acids. Optimization of the biological activity was achieved by adopting cyano(m-phenoxyphenyl)methanol as alcoholic part and two

halogen atoms[3] (or polyhalogenomethyl and halogen groups[4]) on the vinylic moiety of the acidic part[5]. Among the numerous variations of the substituents on the vinyl group, very few are known to be vinyl sulphides: esters of 3(arylthio-ethenyl)-2,2-dimethyl-cyclopropanecarboxylic acids have been claimed to show good insecticidal activity[6]. We desired to test the corresponding alkylthio(halogeno)ethenyl- and, possibly, the polyhalogenomethylthio(halogeno)ethenyl derivatives. Of the numerous recent methods[7] for the synthesis of vinyl sulphides, very convenient are Wittig[8] and Wittig-Horner [9]syntheses,but only one report[10] deals with diethyl phenylthio(chloro)methanephosphonate. We reached our goal by using both diethyl alkylthio(halogeno)-methanephosphonates and alkylthio(halogeno)triphenylphosphoranes, obtained "in situ", by a one-pot reaction under phase transfer catalytic conditions. Furthermore we succeeded in synthesizing the diethyl trifluoromethylthio(chloro)methanephosphonate which underwent the Wittig-Horner reaction in the normal way.

RESULTS AND DISCUSSION

Dichloromethylenetriphenylphosphorane is usually obtained from triphenylphosphine and carbon tetrachloride[11](or better bromotrichloromethane[12]) or from chloroform and potassium tert-butoxide[13] : the dichlorocarbene firstly formed is trapped by triphenylphosphine. On the other hand dichlorocarbene can be generated from chloroform and 50% aq.sodium hydroxide solution with a phase transfer catalyst (P.T.C.)[14]; furthermore, several Wittig reactions have been carried out starting from phosphonium salts and bases under P.T.C.conditions[15]. A combination of these procedures has never been described. Actually, by vigorously stirring a chloroform solution of triphenylphosphine, benzaldehyde and a phase transfer catalyst (triethylbenzylammonium chloride, TEBA) with an aq.50% sodium hydroxide solution, at 60°C for 2 h, β,β-dichlorostyrene was obtained (47% yield of isolated product):

$$CHCl_3 + Ph_3P + PhCHO \xrightarrow[TEBA]{50\%\ aq.NaOH} PhCH = CCl_2 + Ph_3PO$$

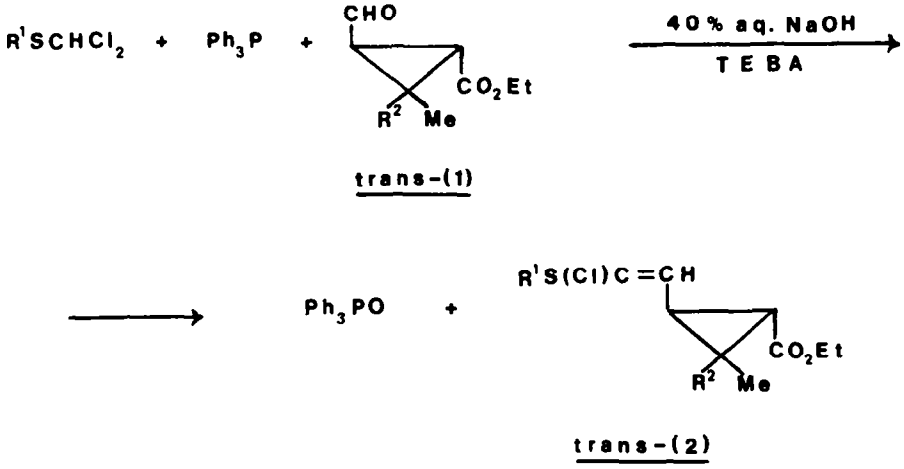
This is an unprecedented example of a one-pot Wittig reaction, carried out under P.T.C. conditions, not starting from a pre-formed phosphonium salt. The reaction is not of general applicability, since it suffers from the competing reactions (like aldol condensation) which undergo many carbonyl compounds under basic conditions. Nevertheless it can be extended to other substrates which generate carbenes by basic treatment and the phosphoranes so obtained "in situ" can react with suitable carbonyl compounds.

α,α-Dichlorodimethylsulfide is unreactive towards triphenylphosphine (practically no reaction after 8 h refluxing in benzene) but is known to give methylthio(chloro)carbene by basic treatment under P.T.C. conditions[16]. Accordingly, when a benzene solution of this dichlorothioether, triphenylphosphine, benzaldehyde and a catalytic amount of TEBA was vigorously stirred, at room temperature for half an hour, with a 40% aq.sodium hydroxide solution, β-methylthio, β-chloro-styrene (E-Z mixture) was obtained (44% yield of distilled product):

$$MeSCHCl_2 + Ph_3P + PhCHO \xrightarrow[TEBA]{40\%\ aq.NaOH}$$

$\longrightarrow$ PhCH = C(Cl)SMe + Ph_3PO

The reaction proved to be practicable when the aldehyde group was linked to a cyclopropane ring and so could be used for the synthesis of new pyrethroids. Thus, by reacting under the above conditions, α,α-dichlorodimethylsulfide with the ethyl esters of the trans-2-methyl, 3-formyl-cyclopropanecarboxylic acid and the corresponding 2,2-dimethyl derivative (trans-caronaldehyde ethyl ester), the expected alkenes (E-Z mixture) were obtained in satisfactory yield (61 and 68% respectively). With $PhSCHCl_2$ and iso-$BuSCHCl_2$, and trans-caronaldehyde ethyl ester the yields were modest (34 and 31% respectively); in the case of $PhSCHCl_2$, which did not react under the usual mild conditions, the reaction mixture was refluxed for 6 h, so performing at the same time the ester saponification. The obtained alkenes were converted to pyrethroids through hydrolysis of the ethyl esters, acid chloride formation and esterification with cyano(m-phenoxyphenyl)methanol:



R^1 = Me, i-Bu, Ph; R^2 = H,Me

i:KOH(MeOH); ii: $SOCl_2(CH_2Cl_2)$; iii: m-$PhOC_6H_4CH(CN)OH$

α,α-Dibromodimethylsulfide[17] is more liable than α,α-dichlorodimethylsulfide to alkaline hydrolysis and therefore for the synthesis of trans-(2)(R^1=R^2=Me, Br instead of Cl) we preferred to use the Wittig-Horner reaction of the corresponding diethylphosphonate, obtained from the same dibromosulfide by a modification of the procedure[18a] known for the chloro-derivative:

$MeSCHBr_2 + P(OEt)_3 \longrightarrow$

$\longrightarrow MeSCHBrP(O)(OEt)_2$ (3)

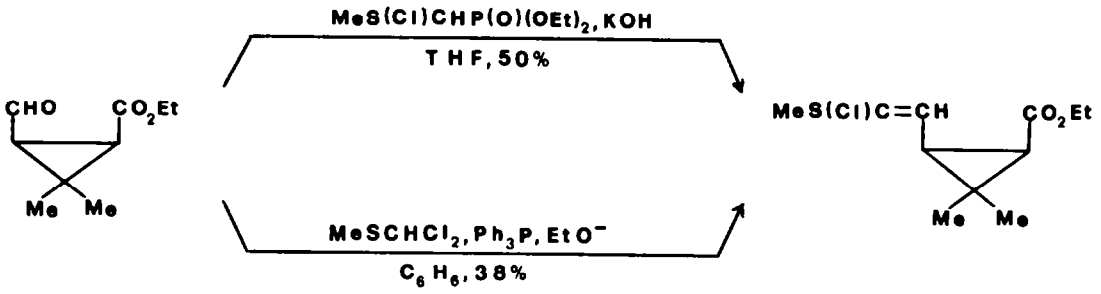
(3) + trans-(1)(R^2=Me) $\longrightarrow$

$\longrightarrow$ trans-(2)(R^1=R^2=Me;Br instead of Cl)

Cis-caronaldehyde ethyl ester is less reactive than the trans- isomer towards the Wittig reagent and therefore can suffer from the concurrent alkaline

hydrolysis to a greater extent than the trans isomer under the same experimental conditions. For this reason diethyl methylthio(chloro)methanephosphonate[18] may be in this case the reagent of choice: it gave cis-(2) (R^1=R^2=Me), E-Z mixture, in 50% yield.

Both the hydrolysis of the cis-caronaldehyde ethyl ester and the previous preparation of the phosphonate were avoided in another way: by using sodium ethoxide (from ethanol and sodium hydride) as base in the calculated amount necessary to convert the dichlorothioether, cis-(2) (R^1=R^2= Me), E-Z mixture, was obtained, though in 38% yield only:



The cis and trans pyrethroids obtained from the intermediate(2), (i.e., the cyano(m-phenoxyphenyl)methyl esters instead of the ethyl esters) showed interesting insecticidal activity, especially against Musca domestica[19].

Next we considered it worth the corresponding trifluoromethylthio derivatives. When CF_3SCH_2Cl[20] was treated, in the presence of benzaldehyde, in the same manner as $MeSCHCl_2$, no alkene was obtained:

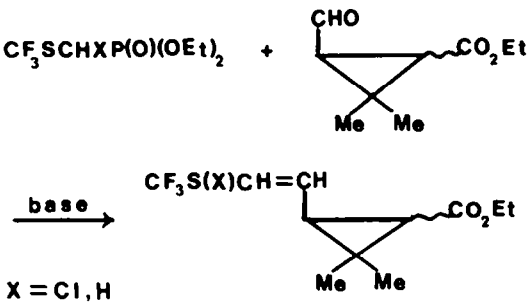
$$CF_3SCH_2Cl + Ph_3P + PhCHO \xrightarrow[TEBA]{40\%\ aq.NaOH} \text{no alkene}$$

Most probably the carbene CF_3SCH was not formed, owing to decomposition of the intermediate carbanion (CF_3^- is a good leaving group). Then we turned our attention to the corresponding phosphonates, but $CF_3CHXP(O)(OEt)_2$ (X = H,Cl) were not known. The synthesis of diethyl trifluoromethyl(chloro)metanephosphonates was carried out through addition[21] of the corresponding sulfenyl chloride to diethyl diazomethanephosphonate[22]:

$$CF_3SCl + N_2CHP(O)(OEt)_2 \longrightarrow CF_3SCHClP(O)(OEt)_2 + N_2$$

The diethyl trifluoromethylthio(chloro)methanephosphonate prepared in this way (69% yield), underwent the Wittig-Horner reaction with caronaldehyde ethyl ester (cis-trans mixture) to give a mixture of three alkenes: trans, E and Z isomers, and cis, one isomer alone (E or Z?)(total yield: 50%). The same phosphonate was also reduced (Zn/AcOH) and the new diethyl trifluoromethylthio-methane-

phosphonate underwent the Wittig-Horner reaction equally well (55% yield):



These alkenes were subsequently converted into the usual cyano (m-phenoxyphenyl)methyl esters which showed moderate insecticidal activity.

EXPERIMENTAL

M.p.s. were determined on a Büchi apparatus and are uncorrected. I.r. spectra were obtained on a Perkin-Elmer instrument Model 21. ^{1}H N.m.r. spectra were recorded on a Bruker WP80 SY spectrometer in ^{2}H chloroform solutions with Me_4Si as internal standard. For gas-liquid chromatography (g.l.c.) a Dani 360 instrument was used, equipped with a 2 m X 3 mm i.d. column packed with 3% OV 17 on Chromosorb W AW-DMCS or with 3% SP 2340 on 100/120 Supelcoport. Mass spectra were obtained on a Finnigan 4021 spectrometer equipped with an INCOS Data System.

Caronaldehyde ethyl ester (cis and trans isomers, as well as their mixture) was supplied by Farmoplant. The other reagents were commercial products and were used as obtained without further purification.

1. β,β-Dichlorostyrene.

A mixture of triphenylphosphine (13.1 g, 0.05 mol), benzaldehyde (5.3 g, 0.05 mol), triethylbenzylammonium chloride (TEBA)(0.23 g, 1 mmol) in chloroform (60 ml) and sodium hydroxide (20 g, 0.5 mol) in water (20 ml) was vigorously stirred at 60°C for 2 h. The mixture became light brown. After cooling to room temperture, water (20 ml) was added and the organic phase separated off. The aq.solution was extracted with chloroform (2 x 100 ml), the chloroform solutions combined, washed with water (50 ml), dried (Na_2SO_4) and evaporated under reduced pressure. Addition of diethyl ether (100 ml) to the crude oil separated triphenylphosphine oxide (7 g). Evaporation of the etheral solution left a residue which was purified by flash chromatography (eluant, hexane-ethyl acetate, 3:1) (4.0 g, 46.5% yield). The β,β-dichlorostyrene was identified by comparison with an authentic sample[13]. No effort was made to increase the yield.

2. β-Methylthio, β-chlorostyrene.

40% Aq.sodium hydroxyde (15 ml) was added dropwise with vigorous stirring, to a solution of α,α-dichlorodimethylsulfide (6.6 g), 0.05 mol), benzaldehyde (5.3 g, 0.05 mol) and triethylbenzylammonium chloride (TEBA, 0.23 g, 1 mmol) in benzene (25 ml). The temperature rose from 20° to 30°C and remained at this point for 30 min, while the mixture became gradually brown coloured. Benzene (40 ml) and water (40 ml) were added to enable easy phase separation. The organic phase was washed with water (30 ml), dried (Na_2SO_4) and evaporated under reduced pressure. The thick oily residue was treated with ethyl ether (50 ml) and the triphenylphosphine oxide (11 g) separated. The ethereal solution was evaporated and the residue distilled in vacuo collecting

the central crop, boiling at 112-115°C/ 1.5 mmHg (3.8 g, 44% yield) (Found: C,58.32; H,4.75;Cl,19.23; S, 17.79. C_9H_9ClS requires C,58.54; H,4.88; Cl,19.24; S,17.34%); δ ($CDCl_3$) 2.37 and 2.38 (3H,s,Me,E-Z isomers), 6.80 and 6.92 (1H,s,vinylic H, E-Z isomers), 7.15-7.65 (5H,m,Ar).

3. Ethyl 3(2-chloro,2-methylthio-ethenyl)-2-methyl-cyclopropanecarboxylate (trans).

The same procedure given in 2 was used for the reaction of α,α-dichlorodimethylsulfide with ethyl 3-formyl, 2-methyl- cyclopropanecarboxylate (predominantly trans[23], 0.045 mol). The resulting oil was distilled, b.p. 117-119°C/ 1.5 mmHg (6.5 g, 62% yield) (Found: C,51.46; H,6.48; Cl,14.91; S,14.04.$C_{10}H_{15}ClO_2S$ requires C,51.14; H,6.44; Cl,15.13; S,13.64%); ν max 1725 (CO) and 1600 (weak, double bond) cm^{-1}; δ($CDCl_3$) 1.25 (s,Me), 1.26 (t,Me-CH_2) and 1.20-1.40 (m,2-H): these signals taken all together integrated for 7H, 1.65-1.85 (1H,m,1-H), 2.32 and 2.34 (s,SMe, E-Z isomers) together with 2.20-2.40 (m,3-H) integrated for 4H, 4.18 (2H,q,Me-CH_2), 5.46 and 5.48 (1H,d,J=9Hz, vinylic H, E-Z isomers).

4. Ethyl 3(2-chloro, 2-methylthio-ethenyl)-2,2-dimethyl-cyclopropanecarboxylate (trans).

By the same procedure given in 2, starting from trans-caronaldehyde ethyl ester (0.016 mol), a crude oily residue was obtained (3.1 g) which could be purified by flash chromatography (eluant, hexane-ehyl acetate, 4:1) to afford the expected alkene (2.7 g, 68% yield); ν max 1725 (CO) and 1590 (weak, double bond) cm^{-1}; δ ($CDCl_3$) 1.12-1.36 (9H,m,2-Me together with CH_2-Me), 1.58 (1H,d,J=5Hz, 1-H), 2.35 and 2.37 (3H,s, SMe,E-Z isomers), 2.25-2.55 (1H,m,3-H), 4.15 (2H,q,CH_2-Me), 5.69 and 5.70 (1H, d,J=8Hz, vinylic H, E-Z isomers).

5. Cyano(m-phenoxyphenyl)methyl-3(2-chloro,2-methylthio-ethenyl)-2,2-dimethyl-cyclopropanecarboxylate (trans).

The ethyl ester obtained in 4 was hydrolyzed in the usual manner (potassium hydroxide in methanol) treated with thionyl chloride in dichloromethane, to get the acid chloride and finally esterified with cyano(m-phenoxyphenyl)-methanol. The pyrethroid was obtained in 50% total yield; δ($CDCl_3$) 1.10- 1.30 (6H,m,2-Me), 1.59 and 1.60 (1H,d,J=6Hz, 1-H, two diastereoisomers), 2.30-2.50 (1H, m,J=8Hz, 3-H), 5.62 and 5.65 (1H, d,J=8Hz, vinylic H, E-Z isomers), 6.38 and 6.40 (1H,s,CHCN, two diastereoisomers), 6.95-7.50 (9H,m,Ar).

6. Ethyl 3[(2-chloro,2-(2-methyl propyl-thio)-ethenyl]-2,2-dimethylcyclopropanecarboxylate (trans).

By the same procedure given in 2, from dichloromethyl-iso-butylsulphide[24] and trans-caronaldehyde ethyl ester (0.01 mol), a crude oil was obtained which, after evaporation in vacuo of the unreacted aldehyde, was sufficiently pure for the further transformation into the pyrethroid (0.9 g, 31% yield, E-Z mixture); δ($CDCl_3$) 0.95-1.35 (15H,m,Me), 1.58 (1H, d,J=5 Hz,1-H), 1.75 (1H,m,$CHMe_2$), 2.32 (1H,m,3-H), 2.66 and 2.70 (2H,d,J=6.5Hz, CH_2S, E-Z isomers), 4.10 (2H,q,CH_2Me), 5.68 and 5.73 (1H,d,J= 8Hz,vinylic H, E-Z isomers).

7. Cyano(m-phenoxyphenyl)methyl 3(2-

chloro,2-phenylthio-ethenyl)-2,2-dimethyl-cyclopropanecarboxylate (trans).

Dichloromethylphenylsulphide did not react with trans-caronaldehyde ethyl ester under the conditions given in 2 (g.l.c. control). Therefore the reaction mixture (13.5 mmol of aldehyde) was refluxed for 6 h. After separation from the aq.phase, the organic phase was acidified (10% aq.HCl) and extracted with ethyl acetate (2 x 50 ml). Drying (Na_2SO_4) and evaporation of the solvent left a white solid, m.p. 108- 109°C (1.3 g, 34% yield). This acid, treated with thionyl chloride and then esterified with cyano(m-phenoxyphenyl)methanol, gave the final pyrethroid. δ ($CDCl_3$) 1.15-1.30 (6H,m,2-Me), 1.68 (1H,d,J= 4.5Hz, 1-H), 2.45-2.70 (1H,m,3-H), 5.90 and 5.91 (1H,d,J=9Hz,vinylic H, E-Z isomers), 6.35 and 6.36 (1H, s, CH-CN, two diasteroisomers), 6.95-7.50 (14H,m, Ar).

8. Ethyl 3(2-bromo,2-methylthio-ethenyl)-2,2-dimethyl-cyclopropanecarboxylate (trans).

Diethyl methylthio(bromo)methanephosphonate was prepared by a modification of the procedure given[18a] for the corresponding chloroderivative. α,α-Dibromodimethylsulfide[17] (3.08 g, 0.014 mol) was added to triethylphosphite (2 ml, 0.0117 mol) without any solvent, under nitrogen atmosphere with magnetic stirring. The solution was slowly heated to 60°C and stirring was continued at this temperature for 2 h. Water (10 ml) was added and the mixture extracted with ethyl ether (2 x 10 ml). The ethereal solution was washed with water, dried (Na_2SO_4) and evaporated. An oily residue was left (2.92 g, 90% yield) which decomposed on attempted distillation (150°C/ 4.5 mmHg), but, at a g.l.c. control, proved to be sufficiently pure and as such was subsequently used. To a solution of this phosphonate (2.8 g, 0.01 mol), trans-caronaldehyde- ethyl ester (1.70 g, 0.01 mol) and TEBA (0.11 g, 0.5 mmol) in benzene (20 ml) was added 50% aq.sodium hydroxide (4 ml) with vigorous stirring. After stirring for 30 min, water (40 ml) and benzene (40 ml) were added to enable easy phase separation. The slightly brown organic phase was filtered through a layer (4 cm) of silica gel, washing with ethyl ether. Evaporation of the combined organic solutions left an oil which was purified by flash chromatography (eluant, hexane-ethyl acetate, 5:1)(1.2 g, 41% yield); ν max 1730 (CO) cm^{-1}; m/e 292-294 (M^+), 277-279 (M-Me), 219-221 (M-CO_2Et), 213 (M-Br), 203-205, 197, 185, 167, 155, 140 (219-221-Br).

9. Ethyl 3(2-chloro,2-methylthio-ethenyl)-2,2-dimethyl-cyclopropanecarboxylate (cis).

A. To a suspension of finely powdered 85% potassium hydroxide (0.9 g, 0.013 mol) in anhydrous THF (5 ml) was added, with stirring at room temperature, a solution of diethyl methylthio(chloro)-methanephosphonate[18] (1.2 g, 5 mmol) and cis-caronaldehyde ethyl ester (0.85 g, 5 mmol) in anhydrous THF (5 ml). The temperature of the mixture rose from 20° to 30°C. After 30 min stirring, n-hexane (20 ml) was added, the mixture was filtered through a layer (4 cm) of silica gel, eluting with ethyl ether. The solution was evaporated and the residue heated in vacuo (1.5 mmHg) to remove the unreacted aldehyde. A pale yellow oil was left (0.7 g, 50% yield);

$\delta(CDCl_3)$ 1.25 (3H,t,J=8Hz CH_2-Me), 1.26 (6H,s,2-Me), 1.77 and 1.78 (1H,d,J=8Hz, 1-H, E-Z isomers), 2.0-2.30 (1H,m, 3-H,E-Z isomers), 2.25 (3H,s,SMe), 4.11 (2H,q, J=8Hz,CH_2-Me), 6.30 and 6.32 (1H,d,J=8Hz,vinylic H, E-Z isomers). The same reaction with trans-caronaldehyde ethyl ester gave analogous results. However g.l.c. analysis (OV17 column, programmed temperature: 100 ⟶ 250°C, 10°C/min, carrier gas nitrogen, 24 ml/min) revealed a different ratio of E-Z isomers, but we did not identify which was which.

B.A solution of α,α-dichlorodimethylsulfide (2.8 g, 0.021 mol), cis-caronaldehyde ethyl ester (3.4 g, 0.02 mol) and ethyl alcohol (0.6 ml, 0.01 mol), in benzene (20 ml) was dropped, with stirring at 5°C, into a suspension of sodium hydride (0.6 g of 80% dispersion in mineral oil, 0.02 mol) and triphenylphosphine (5.24 g, 0.02 mol) in dry benzene (20 ml). The reaction was exothermic, but the temperature was kept below 10°C by external cooling. After heat evolution ceased, the mixture was stirred an additional hour at room temperature. Ethyl ether (40 ml) was added and the solution filtered through a layer (4 cm) of silica gel. Evaporation of the solvents and purification of the crude residue by flash chromatography (eluant, hexane-ethyl acetate, 10:1) afforded the same alkene obtained in A, E-Z mixture (1.9 g, 38% yield).

10. Diethyl trifluoromethylthio(chloro)-methanephosphonate.

A solution of diethyl diazomethanephosphonate[22] (6.80 g, 0.038 mol) in dry dichloromethane (100 ml) was added, with magnetic stirring at -20°C, to a solution of trifluoromethanesulphenyl chloride (7.7 g, 0.056 mol, as estimated to be contained, together with bis(trifluoromethyl)disulphide, in 11.5 g of the mixture obtained according to Kühle[25]). The cooling bath was removed; the temperature gradually rose to 20°C and stirring was continued at this temperature for 6 h. After this time a sample no longer showed the peak of diazomethanephosphonate (2110 cm^{-1})[22]. The reaction mixture was evaporated under reduced pressure [bis(trifluoromethyl)disulphide boils at 31-37°C]. An oil was left (7.50 g, 69% yield with respect to phosphonate) which, after purification by column chromatography on silica gel (eluant, hexane-ethylacetate, 1:1) gave a pure product (g.l.c. analysis, SP2340 column, programmed temperature: 100 ⟶ 260°C, 10°C/min, carrier gas nitrogen, 24 ml/min, 8 min retention time). (Found: C,25.51; H,3.79; Cl,12.14; F,18.92; S,11.54. $C_6H_{11}ClF_3O_3PS$ requires C,25.12; H,3.87; Cl,12.39; F,19.89; S,11.16%).

11. Ethyl 3(2-chloro, 2-trifluoromethylthio-ethenyl)-2,2-dimethyl-cyclopropanecarboxylate (cis-trans mixture).

A solution of diethyl trifluoromethylthio(chloro)methanephosphonate, obtained in 10 above, (0.57 g, 2 mmol) and caronaldehyde ethyl ester (cis-trans mixture, 30:70)(0.34 g, 2 mmol) in dry toluene (10 ml) was added dropwise to a suspension of sodium hydride (0.2 g of 80% dispersion in mineral oil, 6.7 mmol) in dry toluene (5 ml), with magnetic stirring at room temperature. After hydrogen evolution ceased, the mixture was stirred for additional 30 min. Addition of ethyl ether separated mineral salts (sodium diethylphosphate and excess sodium hydride). The mixture was

filtered through a layer (4 cm) of silica gel eluting with ethyl ether-hexane (1:1) and the solution evaporated under reduced pressure. A pale yellow oil was obtained (0.50 g). A g.l.c. control (OV 17 column, programmed temperature: 100 ⟶ 260°C, 10°C/min, carrier gas nitrogen, 24 ml/min) revealed that unreacted starting aldehyde and phosphonate were still present in addition to three reaction products: trans, E and Z isomers (about 14 min retention time) and cis (13 min retention time). This result was confirmed by carrying out the same reaction with the cis-aldehyde: only one isomer (E or Z?) was formed in this case. The crude oil was then purified by flash chromatography (eluant, hexane-ethyl acetate, 10:1) collecting a pale yellow oil (0.30 g, 50% yield); ν max 1725 (CO), 1600 (weak, double bond) and 755 (bending of SCF_3) cm^{-1}. A further flash chromatography (eluant, hexane-ethyl acetate, 15:1) allowed separation of trans (E-Z mixture) and cis isomers: the cis isomer was eluted first. GC-MS (2 mt x 2 mm i.d.SE 30 column, programmed temperature: 120 (2 min) ⟶ 125°C (hold), 2°C/min, carrier gas helium, 10 ml/min), trans-isomer, m/e 302 (M^+), 287 ($M-CH_3$) 257 (M-EtO), 229 ($M-CO_2Et$), 159. The cis isomer showed essentially the same spectrum.

12. Cyano(m-phenoxyphenyl)methyl 3(2-chloro,2-trifluoromethylthio-ethenyl)-2,2-dimethyl-cyclopropanecarboxylate (cis).

The ethyl ester, cis-isomer, isolated as indicated in 11, was transformed, in the usual manner, into the pyrethroid, which was purified by flash chromatography (eluant, hexane- ethylacetate, 10:1); δ ($CDCl_3$) 1.20-1.40 (6H,m,2-Me), 1.90- 2.50 (2H,m,1-H+3-H), 6.37 and 6.41 (1H,s,CHCN,two diastereoisomers), 6.90 (1H,d,J=6Hz, vinylic H), 7.0-7.50 (9H, m,Ar).

13. Diethyl trifluoromethylthiomethanephosphonate.

A mixture of diethyl trifluoromethylthio(chloro)methanephosphonate, prepared as indicated in 10, (2.87 g, 0.01 mol) was heated at 80°C for 3 h. After filtration, the solution was evaporated under reduced pressure. Addition of ethyl ether (5 ml) separated other solid materials which were filtered off. The ethereal solution was washed with aq.sodium hydrogencarbonate until neutral and then with water, dried (Na_2SO_4) and evaporated. It left an oil (1.4 g, 56% yield); (ν max 757 (bending of SCF_3) cm^{-1}; the chlorine was no longer present) which was used directly for the following reaction.

14. Cyano(m-phenoxyphenyl)methyl 3(2-trifluoromethylthio-ethenyl)-2,2-dimethyl-cyclopropanecarboxylate (cis-trans mixture).

By operating exactly as in 11 above, with the diethyl trifluoromethylthiomethanephosphonate prepared in 13, starting from 5 mmol of caronaldehyde ethyl ester (cis-trans mixture, 30:70), the intermediate alkene was obtained in 55% yield of purified product; ν max 1730 (CO), 1610 (weak, double bond) and 755 (bending of SCF_3) cm^{-1}. It was converted to the pyrethroid by the usual sequence; ν max 1735 (CO), 755 (SCF_3) cm^{-1}; δ ($CDCl_3$) 1.10-1.30 (6H,m,2-Me), 1.60-2.40 (2H,m,1-H+3-H), 5.55-6.40 (3H,m,vinylic H+CHCN), 6.90-7.45 (9H,m,Ar).

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