Studies on Chrysanthemate Derivatives. VI.[1] A Stereoselective Synthesis of *trans*-3-(2,2-Dichlorovinyl)-2,2-dimethyl-1-cyclopropanecarboxylic Acid and Related Compounds

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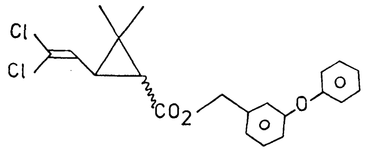
(Received October 7, 1978)

A new method is described for the stereoselective synthesis of *trans*-3-(2,2-dichlorovinyl)-2,2-dimethyl-1-cyclopropanecarboxylic acid (**2t**) *via* ethyl 3,3-dimethyl-4,6,6,6-tetrachlorohexanoate (**3a**) as a key intermediate. The key intermediate (**3a**) was obtained by addition of carbon tetrachloride to ethyl 3,3-dimethyl-4-pentenoate, prepared by condensation of 3-methyl-2-buten-1-ol and triethyl orthoacetate followed by Claisen rearrangement. Treatment of **3a** with sodium *t*-pentyloxide in benzene gave ethyl *trans*-2,2-dimethyl-3-(2,2,2-trichloroethyl)-1-cyclopropanecarboxylate (**6t**) in good yield. Dehydrochlorination and hydrolysis of **6t** using potassium hydroxide in ethanol afforded **2t** in high yield.

Natural pyrethrins and related synthetic pyrethroids, which consist mainly of furylmethyl and cyclopentenyl derivatives as alcohol moieties and chrysanthemic acid as acid moiety, are unstable in air and light.[3] This property restricts their use, particularly against agricultural pests, in spite of their outstanding potency against many insect species and low mammalian toxicity. 3-Phenoxybenzyl alcohol was discovered by the Sumitomo group to be useful as an alcohol moiety of pyrethroids and the benzyl chrysanthemate (phenothrin) had been known to be relatively resistant to photo-irradiation.[4] Its stability, however, has been assessed to be still insufficient for agricultural use. Recently, Elliott and his coworkers have found a new pyrethroid, 3-phenoxybenzyl 3-(2,2-dichlorovinyl)-2,2-dimethyl-1-cyclopropanecarboxylate (**1**; permethrin) which showed adequate stability in light and air, prominent insecticidal activity, and low mammalian toxicity.[5] This breakthrough focused attention on the potential of synthetic pyrethroids in agricultural pest control. Further detailed investigation on permethrin (**1**) has clarified that the *trans*-isomer of **1** was much less toxic to mammals than the *cis*-isomer.[6]

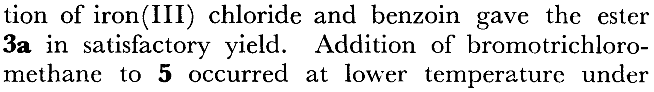


Permethrin (**1**)

The acid moiety of permethrin (**1**), 3-(2,2-dichlorovinyl)-2,2-dimethyl-1-cyclopropanecarboxylic acid (**2**; dichlorovinylchrysanthemic acid), was originally synthesized by Farkas *et al.*[7] by cyclopropanation of 1,1-dichloro-4-methyl-1,3-pentadiene with ethyl diazoacetate. Alternatively, the acid (**2**) was prepared by ozonolysis of the parent chrysanthemate followed by condensation of the resulting 2,2-dimethyl-3-formyl-1-cyclopropanecarboxylate with dichloromethylenetriphenylphosphorane.[8]

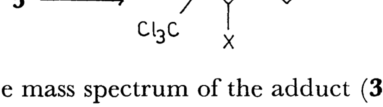
These methods, however, provide less satisfactory results from an industrial point of view concerning yield, stereoselectivity of the cyclopropanecarboxylate formation, and cost. Under these considerations, the stereoselective synthesis of **2** deserves high priority.[9] In this report, we describe a new stereoselective synthesis of the *trans*-isomer (**2t**)[10] *via* ethyl 3,3-dimethyl-4,6,6,6-tetrachlorohexanoate (**3a**) as a key intermediate.[11]

3-Methyl-2-buten-1-ol (**4**) was prepared by allylic rearrangement of 2-methyl-3-buten-2-ol in the presence of acetic acid and acetic anhydride followed by hydrolysis with aqueous sodium hydroxide in good yield. Condensation of **4** and triethyl orthoacetate followed by Claisen rearrangement under catalysis of propionic acid gave ethyl 3,3-dimethyl-4-pentenoate (**5**) in 54% yield according to the procedure of Johnson *et al.*[12]



4 **5**

Addition reaction of haloalkanes such as carbon tetrahalides and haloforms to olefins using transition metal halides as catalysts was applied to elongation of the vinyl chain in **5** by trichloromethyl group.[13] In addition of carbon tetrachloride to **5**, the combination of iron(III) chloride and benzoin gave the ester **3a** in satisfactory yield. Addition of bromotrichloromethane to **5** occurred at lower temperature under the same catalyst to give ethyl 4-bromo-3,3-dimethyl-6,6,6-trichlorohexanoate (**3b**) in moderate yield.



3a; X=Cl
3b; X=Br

The mass spectrum of the adduct (**3a**) showed molecular peaks at m/e (relative intensity): 314 (1), 312 (4), 310(9), and 308 (7) suggesting a 1 : 1 adduct between **5** and carbon tetrachloride. The NMR spectrum of **3a** showed two doublets at 2.28 (1H; J=15.1 Hz) and 2.53 ppm (1H; J=15.1 Hz) assignable to nonequivalent methylene protons adjacent to the carboxyl group, and three doubleting doublets at 3.08 (1H; J=6.3 and 16.2 Hz), 3.22 (1H; J=2.8 and 16.2 Hz), and 4.40 ppm (1H; J=2.8 and 6.3 Hz) assignable to nonequivalent two methylene protons and the chloromethine proton, respectively.

Cyclization of **3a** was conducted with the use of a variety of bases (Table 1). The distribution of reaction products substantially depends on the employed bases: sodium *t*-pentyloxide in *t*-pentyl alcohol

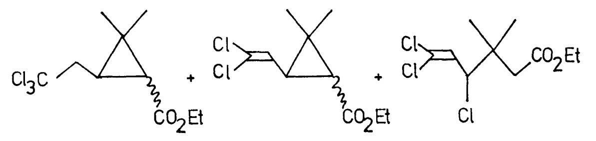
TABLE 1. CYCLIZATION OF ETHYL 3,3-DIMETHYL-4,6,6,6-TETRACHLOROHEXANOATE (**3a**) WITH VARIOUS BASES

Run No	Base (2 mmol)	Solvent	Time (h)[a]	Yield (%) **6** *cis*	*trans*	**7** *cis*	*trans*	**8**
1	EtONa[b]	EtOH	16	>1	1	>1	2	14
2	t-$C_5H_{11}ONa$	t-$C_5H_{11}OH$	2	24	41	2	5	—
3	NaH[c]	DMF	4	5	10	>1	>1	>1
4	$NaNH_2$[d]	DMF	4	1	8	>1	>1	48
5	DBU	THF	16	—	—	—	—	75

a) Reaction temperature: room temperature. b) The starting material (**3a**) was recovered in 67% yield. c) A complex mixture which was not separated was obtained in about 60% yield. d) An unidentified product was obtained in about 20% yield.

gave the cyclized products in good yield, *i.e.*, ethyl 2,2-dimethyl-3-(2,2,2-trichloroethyl)-1-cyclopropanecarboxylate (**6**) as a main product and ethyl dichlorovinylchrysanthemate (**7**), the product of further elimination, as a minor one, whereas the reaction with sodium ethoxide, sodium amide, and 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) in the solvents listed in Table 1 only resulted in the formation of the dehydrochlorinated compound, ethyl 3,3-dimethyl-4,6,6-trichloro-5-hexenoate (**8**).

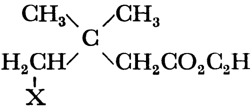
3a ——→



6 **7** **8**

Furthermore scrutiny of cyclization of **3a** and **3b** was made with various solvents using sodium *t*-pentyloxide as a base (Table 2). In cyclization of the chloride (**3a**), the use of benzene, a less polar aprotic solvent, furnished stereoselectively *trans*-cyclization products (**6t** and **7t**), whereas the use of polar solvents such as dioxane, ether, and tetrahydrofuran (THF) increased the amount of *cis*-cyclization products (**6c** and **7c**). In particular the use of THF as a solvent gave predominantly the products of further elimination (**7c** and **7t**) and the total ratio of *cis*/*trans* (**6c**+**7c**/**6t**+**7t**) was nearly 1 : 1. Eventually combination of inverse addition of the base and controlled reaction temperature provided the maximal ratio of *trans*- and *cis*-isomer (Run 2). However, the cyclization of the bromide (**3b**), even in a less polar aprotic solvent such as benzene, proved to be less stereoselective, resulting in a ratio of 3 : 5 (**6c** and **6t**). The results suggest that the *cis*/*trans* ratio of the product (**6**) depends to a great extent on both the polarity of the solvents and the leaving groups (Cl or Br). Presumably in a less polar aprotic solvent the cyclization of the chloride (**3a**) may proceed by bimolecular 1,3-elimination reaction (E2), prefering *anti*-parallel elimination to *syn*-elimination. On the other hand, in a polar solvent it may proceed by unimolecular 1,3-elimination reaction (E1), leading to a mixture of *cis*- and *trans*-isomers. There would be three conformers (**A**, **B**, and **C**) in the chloride **3a**, among which, however, the conformer **C** would be unfavorable because of nonbonded dipole-dipole interaction between the carbonyl group and the chlorine atom. Of the conformers **A** and **B**, the conformer **A** undergoes cyclization smoothly by bimolecular *anti*-parallel 1,3-elimination of hydrogen chloride in a less polar aprotic solvent to lead to the *trans*-isomer, while the conformer **B** does not cyclize in a such manner because of its having no hydrogen *anti*-parallel to the chlorine atom. The *cis*-isomer would be formed by *syn*-1,3-elimination of the conformer **A** and/or unimolecular 1,3-elimination, which is likely in polar aprotic solvents. Under the same conditions as the case of the chloride (**3a**), the bromide (**3b**) tended to increase the *cis*-isomer. Since the reactivity of the bromine atom as a leaving group is much higher than that of the chlorine atom, the unimolecular reaction may significantly compete with the bimolecular *anti*-parallel 1,3-elimination even in a less polar aprotic solvent such as benzene.

TABLE 2. CYCLIZATION OF ETHYL 3,3-DIMETHYL-4-HALO-6,6,6-TRICHLOROHEXANOATE (**3a**) AND (**3b**) WITH SODIUM *t*-PENTYLOXIDE IN VARIOUS SOLVENTS

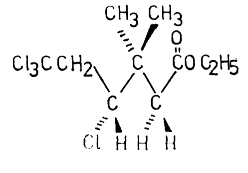


$$Cl_3CCH_2\underset{\displaystyle X}{C}H\text{—}\overset{\displaystyle CH_3\ \ CH_3}{C}\text{—}CH_2CO_2C_2H_5$$

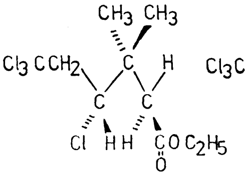
3a: X=Cl, **3b**: X=Br

Run No	X	Solvent[a]	t-$C_5H_{11}ONa$ (mmol)	Yield (%) **6** *cis*	*trans*	**7** *cis*	*trans*
1	Cl	benzene	2	6	69	7	11
2	Cl	benzene[b]	1.5	3	67	5	13
3	Cl	dioxane	2	17	48	14	17
4	Cl	ether	2	24	49	11	12
5	Cl	THF	2	24	15	26	29
6	Cl	THF	5	1	1	47	44
7	Br	benzene	5	29	50	1	1

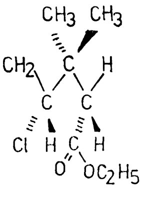
a) Reaction conditions: room temperature for 2 h. b) Inverse addition of the base and reaction at 15—20 °C for 5 h.



A



B



C

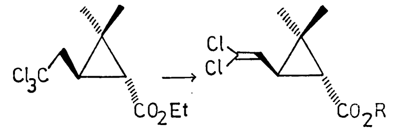
Table 3. Dehydrochlorination of ethyl *trans*-2,2-dimethyl-3-(2,2,2-trichloroethyl)-1-cyclopropanecarboxylate (**6t**)[a]

Run No	Reagent (mmol)	Solvent (ml)	Reaction conditions	Product	Yield (%)
1	KOH (25)	EtOH (30)	55 °C, 20 h	**2t**	92
2	DBU (10)	—	90 °C, 15 min	**7t**	96
3	$ZnCl_2$ (0.5)	—	120 °C, 2 h	**7t**	38

a) Compound **6t** (5 mmol) was used.

The *cis*- and *trans*-isomers of **6** were successfully separated by high pressure liquid chromatography (see Experimental part). In the NMR spectrum (100 MHz), the methine proton adjacent to the carboxyl group on the cyclopropane ring of the *cis*-isomer showed a doublet at 1.66 ppm with a coupling constant of J=8.4 Hz, and the corresponding proton of the *trans*-isomer was observed at 1.36 ppm with a coupling constant of J=5.4 Hz. The fact that the methine proton of the *trans*-isomer appeared at higher field than the *cis*-isomer may be due to the shielding effect of the trichloroethyl group in the same side. Furthermore these assignments are consistent with the values of the coupling constants in *cis*- and *trans*-protons on cyclopropane rings.[14]

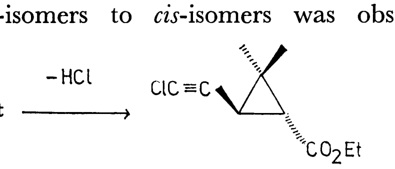
6t



7t; R=Et
2t; R=H

Dehydrochlorination of *trans*-isomer of the ester (**6t**) was examined with several dehydrohalogenation reagents (Table 3). Treatment of **6t** with potassium hydroxide in ethanol and DBU gave the *trans*-acid (**2t**) and the ester (**7t**) respectively in excellent yield. The elimination from **6t** was also effected by zinc chloride to afford **7t** in moderate yield. Under the reaction conditions employed above, no isomerization from *trans*-isomers to *cis*-isomers was observed.

7t



9t

Treatment of **7t** with potassium *t*-butoxide in THF gave ethyl *trans*-3-(2-chloroethynyl)-2,2-dimethyl-1-cyclopropanecarboxylate (**9t**) in good yield.

Experimental

IR spectra were measured on a JASCO IR-A2 Spectrometer. NMR spectra were obtained in a Varian High Resolution NMR Spectrometer A-60 or HA-100 using tetramethylsilane as an internal standard. Chemical shifts are expressed in ppm. Mass spectra were recorded on a Japan Electron Optics Lab. Spectrometer JMS-01SG. All melting and boiling points are uncorrected.

3-Methyl-2-buten-1-ol (4). To a solution of acetic acid (500 ml), acetic anhydride (200 ml), and *p*-toluenesulfonic acid (20 g) was added dropwise a solution of 2-methyl-3-buten-2-ol (88 g) in acetic acid (100 ml) at 20 °C. After stirring for 15 min at room temperature, the mixture was poured into ice-water, neutralized with 10% aqueous potassium hydroxide, and extracted with ether. The extracts were washed successively with 5% aqueous potassium hydroxide and aqueous sodium chloride and dried over anhydrous sodium sulfate. Distillation gave 79 g of 3-methyl-2-butenyl acetate, bp 69—75 °C/53 mmHg (lit,[15]) bp 40—44 °C/15 mmHg). The acetate was hydrolyzed by sodium hydroxide in aqueous methanol to give **4** in 70% yield, bp 65—68 °C/38 mmHg (lit,[15]) bp 45—52 °C/15 mmHg).

Ethyl 3,3-Dimethyl-4-pentenoate (5). The pentenoate **5** was prepared according to the procedure of Johnson *et al.*[12]) A solution of the alcohol **4** (8.6 g), triethyl orthoacetate (81 g), and propionic acid (0.45 g) was stirred at 130—140 °C for 4 h under removing of the resulting ethanol. After cooling, the reaction mixture was washed with saturated aqueous solution of sodium hydrogencarbonate and then with that of sodium chloride, and dried over anhydrous magnesium sulfate. The organic fraction was carefully distilled to give 5.3 g of **5**;[16]) bp 81—83 °C/47 mmHg (lit,[16a]) bp 35—45 °C/0.10 mmHg), IR, $\nu_{\max}^{\text{film}}$ cm^{-1}: 1740, 1645, 1230, and 915, NMR ($CDCl_3$): 1.15 (s, 6H, $2CH_3$), 1.24 (t, 3H; J=7.1 Hz, $\mathrm{OCH_2C\underline{H}_3}$), 2.31 (s, 2H, CH_2CO_2), 4.16 (q, 2H; J=7.1 Hz, $\mathrm{OC\underline{H}_2CH_3}$), 5.01 (dd, 1H; J=1.5 and 10.4 Hz, $\mathrm{CH{=}C\underline{H}H}$), 5.03 (dd, 1H; J=1.5 and 18.3 Hz, $\mathrm{CH{=}CH\underline{H}}$), and 6.02 (dd, 1H; J=10.4 and 18.3 Hz, $\mathrm{C\underline{H}{=}CHH}$).

Addition of Tetrahalomethane to 5. A mixture of **5** (0.1 mol), carbon tetrachloride (0.3 mol), isopropyl alcohol (0.2 mol), iron(III) chloride (0.01 mol), benzoin (0.01 mol), and diethylamine hydrochloride (0.015 mol) was heated under nitrogen at 70—80 °C for 8 h. After cooling, the mixture was diluted with 1% hydrochloric acid and extracted with chloroform. The extracts were dried over anhydrous magnesium sulfate and evaporated *in vacuo* to give a residue, which was distilled to afford the 1 : 1 adduct, ethyl 3,3-dimethyl-4,6,6,6-tetrachlorohexanoate (**3a**) in 82% yield, bp 112—117 °C/0.6 mmHg, IR, $\nu_{\max}^{\text{film}}$ cm^{-1}: 1730 and 1200, NMR (CCl_4): 1.10 (s, 3H, CH_3), 1.18 (s, 3H, CH_3), 1.23 (t, 3H; J=7.0 Hz, $\mathrm{OCH_2C\underline{H}_3}$), 2.28 (d, 1H; J=15.1 Hz, $\mathrm{C\underline{H}HCO_2}$), 2.53 (d, 1H; J=15.1 Hz, $\mathrm{CH\underline{H}CO_2}$), 3.08 (dd, 1H; J=6.3 and 16.2 Hz, $\mathrm{ClCHC\underline{H}H}$), 3.22 (dd, 1H; J=2.8 and 16.2 Hz, $\mathrm{ClCHCH\underline{H}}$), 4.11 (q, 2H; J=7.0 Hz, $\mathrm{OC\underline{H}_2CH_3}$), 4.40 (dd, 1H; J=2.8 and 6.3 Hz, $\mathrm{ClC\underline{H}CHH}$), MS, *m/e* (relative intensity) for $C_{10}H_{16}O_2{}^{35}Cl_4$: 314 (1), 312 (4), 310 (9), and 308 (M^+, 7). With the same catalyst as the case of the addition of carbon tetrachloride, bromotrichloromethane and **5** were heated at 35—45 °C for 5 h to give ethyl 4-bromo-6,6,6-trichlorohexanoate (**3b**) in 33% yield, IR, $\nu_{\max}^{\text{film}}$ cm^{-1}: 1730, 1150, and 650, NMR ($CDCl_3$): 1.17 (s, 3H, CH_3), 1.26 (s, 3H, CH_3), 1.27 (t, 3H; J=7.2 Hz, $\mathrm{OCH_2C\underline{H}_3}$), 2.37 (d, 1H; J=15.1 Hz, $\mathrm{C\underline{H}HCO_2}$), 2.65 (d, 1H; J=15.1 Hz, $\mathrm{CH\underline{H}CO_2}$), 3.31 (d, 1H; J=5.0 Hz, $\mathrm{BrCHC\underline{H}H}$), 3.32 (d, 1H; J=3.5 Hz, $\mathrm{BrCHCH\underline{H}}$), 4.15 (q, 2H; J=7.2 Hz, $\mathrm{OC\underline{H}_2CH_3}$), and 4.55 (dd, 1H; J=3.5 and 5.0 Hz, $\mathrm{BrC\underline{H}CHH}$). Found: C, 33.90; H, 4.52; Br, 22.60; Cl, 30.11. Calcd for $C_{10}H_{16}O_2BrCl_3$: C, 33.88; H, 4.54; Br, 22.54; Cl, 30.00%.

Cyclization of 3a and 3b. A solution of **3a** or **3b** (1 mmol) in any one of solvents (1 ml) as listed in Tables 1 and 2 was added dropwise to a solution or suspension of various bases (2—5 mmol) in the same solvent (2—5 ml) at room temperature, with the exception of run 2 in Table 2. In run 2 a solution of sodium *t*-pentyloxide (1.5 mmol) in benzene was added to a solution of **3a** at 10—15 °C. After stirring under the reaction conditions as shown in Tables 1 and 2, the mixture was diluted with ice-water and extracted with ethyl acetate. The extracts were washed with saturated water solution of sodium chloride and dried over anhydrous magnesium sulfate. Evaporation of the solvent *in vacuo* gave a residue, from which yields were determined by analytical GLC (PEG 20 M, 125 °C). *Cis*- and *trans*-isomers of ethyl 2,2-dimethyl-3-(2,2,2-trichloroethyl)-1-cyclopropanecarboxylate (**6**) were separated by high pressure liquid chromatography on a μ-porasil column (Waters Associates Inc.,) using hexane as the eluent; **6t**, IR, ν_{max}^{film} cm^{-1}: 1729 and 1179, NMR ($CDCl_3$) at 100 MHz: 1.21 (s, 3H, CH_3), 1.25 (s, 3H, CH_3), 1.26 (t, 3H; J=7.2 Hz, $OCH_2C\underline{H}_3$), 1.36 (d, 1H; J=5.4 Hz, $CHC\underline{H}CO_2$), 1.73 (broad q, 1H; J=5.8 Hz, $CHHC\underline{H}CH$), 2.72 (dd, 1H; J=6.0 and 15.0 Hz, $C\underline{H}HCH$), 2.77 (dd, 1H, J=6.3 and 15.0 Hz, $CH\underline{H}CH$), 4.08 (q, 2H; J=7.2 Hz, $OC\underline{H}_2CH_3$), MS, *m/e* (relative intensity) for $C_{10}H_{15}O_2{}^{35}Cl_3$: 278 (1), 276 (5.3), 274 (17.1), and 272 (M^+, 12.8) and **6c**, IR, ν_{max}^{film} cm^{-1}: 1725 and 1180, NMR ($CDCl_3$) at 100 MHz: 1.22 (s, 6H, $2CH_3$), 1.23 (t, 3H; J=7.0 Hz, $OCH_2C\underline{H}_3$), 1.48 (dt, 1H; J=5.5 and 8.4 Hz, $CHHC\underline{H}CH$), 1.66 (d, 1H; J=8.4 Hz, $CHC\underline{H}CO_2$), 3.01 (dd, 1H; J=5.5 and 15.2 Hz, $C\underline{H}HCH$), 3.13 (dd, 1H; J=5.5 and 15.2 Hz, $CH\underline{H}CH$), and 4.11 (q, 2H; J=7.0 Hz, $OC\underline{H}_2CH_3$), MS, *m/e* (relative intensity): 278 (1), 276 (3.5), 274 (11.0), and 272 (M^+, 9.7). The mixture of *cis*- and *trans*-ethyl dichlorovinylchrysanthemate (**7**) was separated by column chromatography (silica gel-silver nitrate, hexane/ethyl acetate=100/3); **7t**[7)], IR, ν_{max}^{film} cm^{-1}: 1730, 1620, and 1180, NMR (CCl_4): 1.20 (s, 3H, CH_3), 1.27 (t, 3H; J=7.2 Hz, $OCH_2C\underline{H}_3$), 1.29 (s, 3H, CH_3), 1.53 (d, 1H; J=5.2 Hz, $CHC\underline{H}CO_2$), 2.19 (dd, 1H; J=5.2 and 8.3 Hz, $=CHC\underline{H}CH$), 4.12 (q, 2H; J=7.2 Hz, $OC\underline{H}_2CH_3$), and 5.63 (d, 1H; J=8.3 Hz, $=C\underline{H}CH$) and **7c**[7)], IR, ν_{max}^{film} cm^{-1}: 1725, 1620, and 1190, NMR ($CDCl_3$): 1.26 (s, 6H, $2CH_3$), 1.27 (t, 3H; J=7.1 Hz, $OCH_2C\underline{H}_3$), 1.83 (dd, 1H; J=1.0 and 8.0 Hz, $=CHCHC\underline{H}CO_2$), 2.02 (t, 1H; J=8.0 Hz, $=CHC\underline{H}CH$), 4.11 (q, 2H; J=7.1 Hz, $OC\underline{H}_2CH_3$), and 6.28 (dd, 1H; J=1.0 and 8.0 Hz, $=C\underline{H}CHCH$). Ethyl 3,3-dimethyl-4,6,6-trichloro-5-hexenoate (**8**) was purified by column chromatography on silica gel (hexane/benzene=1/1), IR, ν_{max}^{film} cm^{-1}: 1730, 1612, and 1150, NMR ($CDCl_3$): 1.15 (s, 6H, $2CH_3$), 1.28 (t, 3H; J=7.1 Hz, $OCH_2C\underline{H}_3$), 2.35 (d, 1H; J=14.5 Hz, $C\underline{H}HCO_2$), 2.51 (d, 1H; J=14.5 Hz, $CH\underline{H}CO_2$), 4.21 (q, 2H; J=7.1 Hz, $OC\underline{H}_2CH_3$), 4.98 (d, 1H; J=10.5 Hz, $=CHC\underline{H}Cl$), and 6.13 (d, 1H; J=10.5 Hz, $=C\underline{H}CHCl$), MS, *m/e* (relative intensity) for $C_{10}H_{15}O_2{}^{35}Cl_3$: 278 (1), 276 (7.0), 274 (20.3), and 272 (M^+, 20.4).

Dehydrochlorination of ***6t***. Compound **6t** (5 mmol) was heated with a variety of reagents such as zinc chloride (0.5 mmol), DBU (10 mmol), and potassium hydroxide (25 mmol) under reaction conditions described in Table 3. After the usual work-up, the crude products were chromatographed on silica gel, using benzene and benzene–ethyl acetate (3/1) as eluents for **7t** and **2t**, respectively. Following spectral data were obtained for **2t**, mp 96—97 °C (lit,[7)] mp 95—96.5 °C), IR, ν_{max}^{Nujol} cm^{-1}: 2700, 1680, and 1620, NMR (CCl_4): 1.23 (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 1.57 (d, 1H; J=5.6 Hz, $CHC\underline{H}CO_2$), 2.25 (dd, 1H; J=5.6 and 8.5 Hz, $=CHC\underline{H}CHCO_2$), 5.61 (d, 1H; J=8.5 Hz, $=C\underline{H}CH$), and 11.97 (broad s, 1H, CO_2H).

Ethyl trans-*3-(2-Chloroethynyl)-2,2-dimethyl-1-cyclopropanecarboxylate (**9t**).* A solution of **7t** (0.21 g) in THF (2 ml) was added dropwise to a slurry of potassium *t*-butoxide (0.22 g) in THF (5 ml) at room temperature. After stirring for 6 hr, the reaction mixture was poured into ice-water and extracted with ether. The extracts were washed with saturated aqueous sodium chloride and dried over anhydrous sodium sulfate. Evaporation of the solvent *in vacuo* gave a residue, which was chromatographed on silica gel (hexane/benzene=1/1) to afford 0.11 g of **9t**, IR, ν_{max}^{film} cm^{-1}: 2220, 1730, and 1175, NMR (CCl_4): 1.20 (s, 3H, CH_3), 1.27 (t, 3H; J=7.1 Hz, $OCH_2C\underline{H}_3$), 1.29 (s, 3H, CH_3), 1.59 (d, 1H; J=5.6 Hz, $CHC\underline{H}CO_2$), 1.85 (d, 1H; J=5.6 Hz, $C\underline{H}CHCO_2$), and 4.12 (q, 2H; J=7.1 Hz, $OC\underline{H}_2CH_3$), MS, *m/e* (relative intensity) for $C_{10}H_{13}O_2{}^{35}Cl$: 202 (1) and 200 (M^+, 2.7).

The authors wish to express their thanks to Dr. K. Murayama for his encouragement and advice and to Dr. N. Soma for his valuable discussion.

References

1) Part V; Y. Nakada, S. Muramatsu, M. Asai, H. Tsuji, and Y. Yura, *Agric. Biol. Chem.*, **42**, 1767 (1978).

2) Present address: 16-47 Sakuradai, Midori-ku, Yokohama-shi, Kanagawa 227, Japan.

3) Y. Chen and J. E. Casida, *J. Agric. Food Chem.*, **17**, 208 (1969).

4) K. Fujimoto, N. Itaya, Y. Okuno, T. Kadota, and T. Yamaguchi, *Agric. Biol. Chem.*, **37**, 2681 (1973).

5) M. Elliott, A. W. Farnham, N. F. Janes, P. H. Needham, D. A. Pulman, and J. H. Stevenson, *Nature*, **246**, 169 (1973).

6) H. Yoshioka and J. Miyamoto, *Kagaku To Seibutsu*, **14**, 549 (1976).

7) J. Farkas, P. Kourim, and F. Sorm, *Collect. Czech. Chem. Commun.*, **24**, 2230 (1959).

8) M. Elliott, A. W. Farnham, N. F. Janes, P. H. Needham, and D. A. Pulman, *Nature*, **244**, 456 (1973).

9) For recent syntheses of the acid **2** and its ethyl ester (**7**) see: a) N. Itaya, T. Matsuo, N. Ohno, T. Mizutani, F. Fujita, and H. Yoshioka, "Synthetic Pyrethroids In ACS Symposium Series 42," ed by M. Elliott, American Chemical Society, Washington, D. C. (1977), p. 45; b) K. Kondo, K. Matsui, and A. Negishi, *ibid.*, p. 128; c) N. Punja, Japan Patent, Kokai, 51-141842 (1976); d) F. Mori, Y. Ohmura, T. Nishida, and K. Itoi, *ibid.*, 51-141843 (1976).

10) We applied for a patent in 1974: Y. Yura, Y. Nakada, and R. Endo, Japan Patent, Kokai, 51-59839 (1976).

11) Kondo *et al.* presented at the 31st National Meeting of Chemical Society of Japan a synthesis of the ethyl ester (**7**) of the acid **2** by a method similar to ours at the nearly same time as we completed our synthesis: K. Matsui, Y. Takahatake, and K. Kondo, Abstracts of Papers, the 31st National Meeting of Chemical Society of Japan, Sendai, October, 1974, Vol. 1, p. 58.

12) W. S. Johnson, L. Werthemann, W. R. Bartlett, T. J. Brocksom, T. Li, D. J. Faulkner, and M. R. Petersen, *J. Am. Chem. Soc.*, **92**, 741 (1970).

13) a) M. Asscher and D. Vofsi, *J. Chem. Soc.*, **1963**, 1887; b) M. Asscher and D. Vofsi, *ibid.*, **1963**, 3921.

14) a) A. F. Bramwell, L. Crombie, P. Hemesley, G. Pattenden, M. Elliott, and N. F. Janes, *Tetrahedron*, **25**, 1727 (1969); b) H. M. Hutton and T. Schaefer, *Can. J. Chem.*, **40**, 875 (1962).

15) T. G. Halsall and A. R. Hands, *J. Chem. Soc.*, **1961**, 3251.

16) a) J. H. Babler and A. J. Tortorello, *J. Org. Chem.*, **41**, 885 (1976); b) K. Kondo, K. Matsui, and Y. Takahatake, *Tetrahedron Lett.*, **1976**, 4359.