Synthesis of Halomethylvinylcyclopropanecarboxylic Acids and Their Esters[†]

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The 3-(2-halo-1-propenyl)-2,2-dimethylcyclopropanecarboxylates were synthesized. They have four diastereoisomers: *E/Z* and *cis/trans* configurations with respect to the 2-halo-1-propenyl side chain and to the cyclopropane ring, respectively. The 3-(2-Chloro-1-propenyl)-2,2-dimethylcyclopropane carboxylates were prepared *via* ethyl 3,3-dimethyl-4,6,6-trichloroheptanoate (2) as a key intermediate and the 2-bromo-1-propenyl derivatives were obtained by the Wittig reaction. The stereochemistry of each of the four diastereoisomers was examined by ¹H NMR spectroscopy.

The *m*-phenoxybenzyl ester of chrysanthemic acid, *i.e.*, phenothrin which was discovered by the Sumitomo group²⁾ in 1973, has been known to be more resistant to photoirradiation than the pyrethroids bearing an other alcohol moiety such as 5-benzyl-3-hydroxymethylfuran or 2-allyl-4-hydroxy-3-methyl-2-cyclopenten-1-one. The photostability of phenothrin, however, has been assessed to be still insufficient under agricultural field conditions. The discovery of the photostable alcohol of *m*-phenoxybenzyl alcohol has led to the development of permethrin and decamethrin (NRDC-161) which have a photostable 2-dihalovinyl-3,3-dimethylcyclopropanecarboxylic acid moiety by Elliott and his co-workers.³⁾ These esters exhibit highly insecticidal activity and relatively low mammalian toxicity as well as photostability, which enable them to be used in agricultural fields such as cotton growing. The *m*-phenoxybenzyl esters of these acids, however, reveal high toxicity to fish, which prohibits their application in paddy fields.⁴⁾

Holmstead⁵⁾ has reported that photooxidation occurs at the *trans* methyl group or the double bond of the isobutenyl substituent in chrysanthemates. Casida⁶⁾ has reported that in housefly and rats the *trans* and *cis* chrysanthemates are hydroxylated by oxidase at the methyl groups of the isobutenyl side chain with subsequent oxidation of the alcohol to the corresponding aldehyde and carboxylic acid successively. Conversely, the 3-dihalovinyl-2,2-dimethylcyclopropanecarboxylic acids have no methyl group to be oxidized on the double bond, but have the double bond photochemically stabilized by two electron-withdrawing halogen atoms; furthermore, the dihalovinyl group not being subjected to oxidation is approximately a biological isosteric group of the isobutenyl substituent of chrysanthemic acid.

From these observations our attention focused on 3-(2-halo-1-propenyl)-2,2-dimethylcyclopropanecarboxylic acid, which is a hybrid structure of chrysanthemic acid and 3-dihalovinyl-2,2-dimethylcyclopropanecar-

[†] Studies on Halomethylvinylcyclopropanecarboxylic Acids and Their Esters. Part III.¹⁾ Halomethylvinylcyclopropanecarboxylic acid is used for 3-(2-halo-1-propenyl)-2,2-dimethylcyclopropanecarboxylic acid as its abridgement.

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FIG. 1.

boxylic acid with respect to the unsaturated side chain. The hybrid acid has four diastereoisomers with respect to the 2-halo-1-propenyl side chain and to the cyclopropane ring *i.e.*, (*E*)-*trans*-, (*Z*)-*trans*-, (*E*)-*cis*- and (*Z*)-*cis*-3-(2-halo-1-propenyl)-2,2-dimethylcyclopropanecarboxylic acids. Interesting features of the hybrid acid are to be expected: (i) the photostability of the 2-chloro-1-propenyl group bearing one halogen atom, (ii) insecticidal activity, especially to insects in paddy fields, and fish toxicity as well as mammalian toxicity, (iii) the *E*- or *Z*-configuration of the methyl group on the double bond with its influence on metabolism. This paper describes the synthesis of each of the four diastereomers of 3-(2-chloro-1-propenyl)-*¹ and 3-(2-bromo-1-propenyl)-2,2-dimethylcyclopropanecarboxylic acid derivatives.*²

RESULTS AND DISCUSSION

Synthesis of four stereoisomers of 3-(2-chloro-1-propenyl)-2,2-dimethylcyclopropanecarboxylic acids and their esters

We have recently reported a synthesis of *cis*- and *trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylic acid *via* ethyl 3,3-dimethyl-4,6,6-tetrachlorohexanoate as a key intermediate.⁷⁾ A similar sequence was

FIG. 2.

applied to the synthesis of the relevant acids. The key intermediate, ethyl 3,3-dimethyl-4,6,6-trichloroheptanoate (**2**), was prepared from 1,1,1-trichloroethane and ethyl 3,3-dimethyl-4-pentenoate (**1**) by radical addition in the coordination sphere using iron (II or III) chloride as a catalyst and organophosphorous compounds as a ligand.⁹⁾ The reaction conditions were examined (Table I).

The cyclization of ethyl 4,6,6-trichloro-3,3-dimethylheptanoate (**2**) with 3 equivalents of sodium *tert*-pentoxide in benzene at room temperature afforded the corresponding *trans*-cyclopropane derivative **3** and its *cis* isomer **4** with the ratio of 85:15 in 86% yields, respectively. The use of tetrahydrofuran as a solvent for the cyclization gave predominantly the *cis* over the *trans* isomer in the ratio of 60:40, respectively. Separation of a mixture of the *cis* and *trans* isomers was successfully achieved by silicagel column chromatography.

The stereochemical assignment of the *cis* and *trans* isomers was made by examining their NMR spectra. The 1-H methine proton of the *cis* isomer **4** adjacent to the ethoxycarbonyl group showed double doublet peaks at 1.48 ppm with a coupling constant of $J = 14.3$ and 1.5 Hz,*³ while the corresponding proton of the *trans* isomer **3** was observed as a doublet at 1.35 ppm with a coupling constant of $J = 5.0$ Hz. The vicinal coupling constant value of *cis* hydrogens is generally observed to be larger than that of the *trans* isomer¹⁰⁾ and, additionally, the observation that the 1-H methine proton of the *trans* isomer **3** appeared at

*¹ Although the activities of the *m*-phenoxybenzyl ester of 3-(2-chloro-1-propenyl)-2,2-dimethylcyclopropanecarboxylic acid against housefly and cockroach were recently reported by Elliott and his co-workers,⁸⁾ neither the method for its preparation nor its stereochemistry was described.

*² The insecticidal activities against green-rice leafhopper and cockroach, and the fish toxicities of four diastereoisomers of each of 2-chloro- and 2-bromo-1-propenyl derivatives will be published in detail in this journal in the near future.

*³ A long range coupling ($J = 1.5$ Hz) with the methylene group was observed.

TABLE I. ADDITION REACTION OF 1,1,1-TRICHLOROETHANE TO ETHYL 3,3-DIMETHYL-4-PENTENOATE (1)

Run. No.	a	b	a/b (mol)	Temp. (°C)	Time (hr)	Y (%)
1	FeCl ₂	P(O)(NMe ₂) ₃	1/2.5	120 ~ 130	18	55 ^a
2	FeCl ₂	P(O)(NMe ₂) ₃	1/5	125 ~ 130	18	70
3	FeCl ₃	P(O)(NEt ₂) ₃	1/5	115 ~ 125	15	60
4	FeCl ₃	P(OEt) ₃	1/5	120 ~ 130	7	33 ^a
5	FeCl ₃	P(OEt) ₃	1/5	120 ~ 130	15	0 ^b

^a The starting material was recovered in 14 and 20% amounts for run 1 and 4, respectively.

^b Decomposed.

FIG. 3.

a: R = C₂H₅, b: R = H, c: R = CH₃

FIG. 4.

a higher field than that of the *cis* isomer 4 may be due to the shielding effects of the 2,2-dichloropropyl group on the same side as the 1-H proton. Dehydrohalogenation of both the *trans* and *cis* isomers (3 and 4) with bases led to the formation of the (*E*)- and (*Z*)- isomers, together with a small amount of the exomethylene product depending on the reaction conditions. Treatment of the *trans* isomer 3 with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) afforded a mixture of the (*E*)-*trans* and (*Z*)-*trans* isomers and the exomethylene products (5a, 6a and 7a) in the ratio of 30:60:10, respectively. The *cis* isomer 4 with DBU or sodium amide in DMSO gave a mixture of the (*E*)-*cis*, (*Z*)-*cis* isomers and the exomethylene product (8a, 9a and 10a) in the ratio of

22:66:11, respectively. The use of sodium hydroxide in methanol in place of DBU for the *cis* isomer 4 afforded no exomethylene product 10b, but only a mixture of the (*E*)- and (*Z*)-*cis* hydrolyzed products (8b and 9b) in the ratio of 61:31, respectively. Under the same reaction conditions, however, the *trans* isomer 3 gave a significant amount of the exomethylene product 7.

The pure (*Z*)-*trans* acid 6b was obtained by hydrolysis of a mixture of the (*E*)- and (*Z*)-*trans* esters (5a and 6a), prepared from the *trans* isomer 3, and followed by fractional recrystallization. The pure (*Z*)-*cis* acid 9b was similarly obtained by hydrolyzing a mixture of the (*E*)- and (*Z*)-*cis* esters (8a and 9a) followed by recrystallization. The (*E*)-*trans* methyl ester

5c was isolated by preparative HPLC from a mixture of the (*E*)- and (*Z*)-*trans* methyl esters (**5c** and **6c**), obtained by treating a mixture of **5b** and **6b** with diazomethane. Isolation by HPLC of the (*E*)-*cis* methyl ester **8c** from the (*E*)- and (*Z*)-*cis* esters was unsuccessful. Alternatively, the (*E*)-*cis* acid **8b** was obtained by the hydrolysis of its *m*-phenoxybenzyl ester **8d** which was separated from a mixture of the corresponding (*E*)- and (*Z*)-*cis* esters (**8d** and **9d**) by silicagel column chromatography. The (*E*)-*trans* *m*-phenoxybenzyl ester **5d** was provided from HPLC by separating a mixture of the (*E*)- and (*Z*)-*trans* esters (**5d** and **6d**) which were obtained by esterification of a mixture of the corresponding acid chlorides with *m*-phenoxybenzyl alcohol. The (*Z*)-*trans* ester **6d** was prepared from the corresponding acid chloride and *m*-phenoxybenzyl alcohol.

Photochemical and acid-catalyzed isomerization

Isomerization related to the double bond and the cyclopropane ring was examined. Photoisomerization of the (*Z*)-*cis* isomer **9a**, using a high pressure mercury lamp in benzene in the presence of benzophenone, afforded the (*E*)- and (*Z*)-*trans* isomers (**5a** and **6a**) along with the starting material **9a**. Isomerization of a mixture of **5a** and **6a** under the same conditions gave a mixture of the (*E*)- and (*Z*)-*cis* isomers (**8a** and **9a**). Thus, photochemical isomerization occurred in both the double bond and the cyclopropane ring.

The Sumitomo group has found the equi-

libration of the *cis*-chrysanthemic acid to the *trans* rich constituent with acetic anhydride in the presence of *p*-toluenesulfonic acid.¹¹ This equilibration may be attained through the enol form of the mixed anhydride formed from the *cis* acid and acetic anhydride. This procedure was applied to the 2-chloro-1-propenyl derivatives. The *cis* acids composed of 17% and 83% of the (*E*)- and (*Z*)-isomers (**8b** and **9b**), respectively, were heated in acetic anhydride in the presence of *p*-toluenesulfonic acid at 140°C to give a mixture of the (*Z*)-*cis*, (*E*)-*trans* and (*Z*)-*trans* isomers (**9b**, **5b** and **6b**) in the ratio of 14:17:69, respectively: the ratio of the *cis* and *trans* isomers in this mixture was 14:86, and the constituents in *Z*- and *E*-configuration were found to be 17:83, respectively. No (*E*)-*cis* isomer **8b** was detected under these isomerization conditions. This suggests that the (*E*)-*cis* isomer **8b** was converted more easily to the (*E*)-*trans* isomer **5b** than the (*Z*)-*cis* isomer **9b**. The constituents in the *E*- and *Z*-configuration preserved their original ratio in the total amount of the *cis* and *trans* isomers. The (*Z*)-*cis* acid **9b** was subjected to isomerization to give a mixture of (*Z*)-*cis* and (*Z*)-*trans* isomers (**9b** and **6b**) with the ratio of 14:86, respectively. These results suggest that the original ratio of the *E*- and *Z*-configuration in the *cis* acids is preserved in both the *cis* and *trans* isomers obtained by this equilibration; therefore, the acid-catalyzed equilibration did occur only with respect to the cyclopropane ring and not to the double bond.

$$\mathbf{8b}:\mathbf{9b}=17:83 \quad \mathbf{8b}:\mathbf{9b}:\mathbf{5b}:\mathbf{6b}=0:14:17:69$$

FIG. 5.

Synthesis of four stereoisomers of 3-(2-bromo-1-propenyl)-2,2-dimethylcyclopropanecarboxylic acids and their esters

The addition reaction of 1,1,1-tribromoethane to ethyl 2,2-dimethyl-4-pentenoate (**1**) resulted in a poor yield of the addition product (**11**) (6~7% yields) under a variety of reaction conditions; therefore, a similar route to the 2-chloro-1-propenyl derivatives was abandoned. Alternatively, a trisubstituted bromoolefin synthesis, utilizing α -bromoalkylidenes according to the method of Smithers,¹²⁾ was applied to the 2-bromo-1-propenyl derivatives. The Wittig reaction of α -bromoethylidenetriphenylphosphorane with methyl *cis*-3-formyl-2,2-dimethylcyclopropanecarboxylate (**12c**) in THF at -45°C afforded a mixture of methyl (*E*)- and (*Z*)-*cis*-3-(2-bromo-1-propenyl)-2,2-dimethylcyclopropanecarboxylates (**13c** and **14c**) in 75% yields, which was then subjected to transesterification with *m*-phenoxybenzyl alcohol in the presence of lithium amide in toluene to give the corresponding benzyl esters of **13d** and **14d** in the ratio of about 3:1 after separation by Lobar column chromatography. On the other hand, the Wittig reaction of the aldehyde of *m*-phenoxybenzyl ester (**12d**) gave a mixture of **13d** and **14d** with the ratio of about 1:1. Analogously, the (*E*)- and (*Z*)-*trans* *m*-phenoxybenzyl esters (**16d** and **17d**) were prepared from the corresponding aldehyde **15d** and α -bromoethylidenetriphenylphosphorane, followed by separation of the resulting mixture of the (*E*)- and (*Z*)-isomers by column chromatography on silicagel.

^1H NMR Analyses of 3-(2-halo-1-propenyl)-2,2-dimethylcyclopropanecarboxylic acids and their derivatives

In the previous paper,¹³⁾ ^{13}C -NMR spectroscopic analysis of 3-(2-chloro-1-propenyl)- and 3-(2-bromo-1-propenyl)-2,2-dimethylcyclopropanecarboxylic acids and their esters synthesized as described above has been reported. ^1H -NMR spectra of each of the four isomers of the 2-chloro-1-propenyl and 2-bromo-1-propenyl derivatives were taken in a solution of tetrachloromethane at 90 or 100 MHz. The analyzed results of the configurations, assignments on the chemical shifts (δ , ppm), spin-spin coupling constants (J , Hz), and the nuclear Overhauser effect (NOE) (%) are summarized in Table II, together with those of the dichlorovinyl and dimethylvinyl analogues as the references with which to be compared.

An assignment of the *E*- and *Z*-configuration on the double bond was mainly based on the NOE of the 1'-H vinyl proton with irradiation at the C-3' and/or C-4' methyl groups. The NOE was carefully measured by irradiating the methyl signals as weakly as possible, because of the close appearance of the methyl groups on the double bond to the 3-H proton on the cyclopropane ring which had strongly coupled with the 1'-H vinyl proton. The NOE values can be divided into two groups: one in the range of 6~13% and the other as almost negligible (see Table II). The compounds with a large NOE are assigned to the *Z*-configuration and the others should be *E*-configuration.

FIG. 6.

In general, the assignment of the protons on the cyclopropane ring, which was poorly substituted, is very difficult by the usual first order approximation method. The NMR spectra of the cyclopropane derivatives present with four substituents, with the exception of the (*E*)-*cis* isomers, are readily analyzed qualitatively by the conventional first-order method. The coupling constants between the 1-H and 3-H (J_{1-3}) positions can be divided into two groups of 8.3~8.7 Hz and 5.2~5.8 Hz. The vicinal coupling constant value of the *cis* hydrogens on a cyclopropane ring is generally observed to be larger than that of the *trans* value.¹⁰⁾ Accordingly, the isomers with larger coupling constant values are assigned to the *cis* configuration and the others with smaller values, to the *trans*. In case of the (*E*)-*cis* isomer, the two protons of 1-H and 3-H appeared relatively close to each other, and additionally coupled with the 1'-H vinyl proton by strong cross-coupling interaction to give a complex pattern. Therefore, a conventional method was not applicable for the analysis of the (*E*)-*cis* isomer, but these characteristic features in the NMR spectrum easily enable it to be distinguished from the other three isomers.

Geminal methyl groups at C-2 on the cyclopropane ring appeared in a relatively narrow region (δ 1.12~1.36). Therefore, the conventional assignment of the two methyl groups, taking into account the shielding or anisotropic effects of the adjacent substituents, was not available. Precise proton spin decoupling experiments together with measurement of the NOE were applied to several derivatives by irradiating the geminal methyl signals as weakly as possible, but sufficiently to detect a certain decoupling effect. These results clarified the ring configuration and the assignment of the geminal methyl groups by long range couplings and NOE results between these methyl groups and the cyclopropane ring protons. NOEs between 3-H and the 4-methyl group for *m*-phenoxybenzyl (*Z*)-*cis*-3-(2-bromo-1-propenyl)-2,2-dimethylcyclopropanecarboxylate (**14d**) and (*E*)-*cis*-3-(2-bromo-1-propenyl)-2,2-dimethylcyclo-

propanecarboxylic acid (**13b**) by irradiation at the C-4 methyl group were $8 \pm 4\%$ and $11 \pm 4\%$, respectively. Irradiation at the C-5 methyl group for these derivatives gave no NOE. Analogously, NOEs of $8 \pm 2\%$ and $7 \pm 2\%$ for the methyl *cis*- and *trans*-3-dichlorovinyl-2,2-dimethylcyclopropanecarboxylates, respectively, were found between 3-H and either the C-4 or C-5 methyl group.

The rotation around the single bond between C-3 and C-1' is strongly restricted both by the 2-halo-1-propenyl group and the geminal methyl groups on the cyclopropane ring, on which the vinyl group lies outside the cyclopropane ring in preferred conformations. For all the compounds in the present studies, the coupling constant $J_{3-1'}$ has relatively large values in the range of 7.2 to 8.6 Hz. This indicates an *s-trans* correlation between 3-H and 1'-H, which is consistent with the above results.

The 1-H proton in the *trans* isomers was observed with smaller couplings in higher fields at about δ 1.39~1.50 than that of the *cis* isomers observed at about δ 1.64~1.76 with larger couplings (*vide supra*). From the preceding discussion and results this may be due to the facts that the 1-H proton in the *trans* isomers is likely to exist above the sp^2 plane of the vinyl group and is mainly shielded by an anisotropic effect of the vinyl group.

The chemical shift of the vinyl proton (1'-H) in both the (*E*)- and (*Z*)-isomers is theoretically considered to be affected by the unresolved induced and anisotropic effects of the halogen atom and methyl substituents on the vinyl group. The vinyl proton of the *cis* isomers, however, always appeared in a lower field (δ 5.76~6.04) than those of the *trans* isomers (δ 5.15~5.57). This may be due to the deshielding effects of the carboxylic acid group in the *cis* isomers in which the acid moiety and the vinyl group are present on the same side of the cyclopropane ring.

It seems that the chemical shifts of the 3-H ring proton are strongly affected by both the configurations of the vinyl group (*Z/E*) and the cyclopropane ring (*cis/trans*) as examined

TABLE II. ¹H-NMR DATA OF CYCLOPROPANECARBOXYLIC ACIDS AND THEIR ESTERS^a

R	3'	4'	Configuration	Chemical shift (ppm)							NOE ^b	Coupling constant (Hz)		
				1	3	4	5	1'	3'	4'		J ₁₋₃	J _{3-1'}	J _{1'-3'/4'}
H	Me	Cl	(Z)-trans	1.45	2.28	1.36	1.19	5.19	2.13	—	7±2%	5.8	8.6	1.4
Me	Me	Cl		1.39	2.20	1.27	1.14	5.18	2.10	—	6±1%	5.4	7.9	1.2
H	Me	Br		1.46	2.23	1.34	1.19	5.37	2.30	—	13±3%	5.5	7.4	1.2
Me	Me	Br		1.41	2.15	1.28	1.16	5.38	2.29	—		5.5	7.5	1.5
H	Cl	Me	(E)-trans	1.48	2.04	1.33	1.23	5.33	—	2.14	0±3%	5.2	7.2	1.4
Me	Cl	Me		1.43	1.96	1.25	1.18	5.32	—	2.15	0±1%	5.4	8.4	1.2
H	Br	Me		1.49	2.03	1.31	1.22	5.57	—	2.30		5.4	8.3	1.4
Me	Br	Me		1.44	1.96	(1.23)	(1.18)	5.54	—	2.30		5.5	8.5	1.4
Me	Me	Me	trans	1.29	1.96	1.24	1.12	4.88	1.70	1.70	7±2%	5.4	7.9	1.3
Me	Cl	Cl	trans	1.50	2.17	1.27	1.19	5.59	—	—		5.4	8.4	—
Me	Me	Cl	(Z)-cis	1.67	2.06	(1.24)	(1.18)	5.76	2.14	—	12±3%	8.7	8.4	1.4
Et	Me	Cl		1.64	2.05	(1.24)	(1.21)	5.77	2.14	—	15±3%	8.7	8.6	1.2
Phb	Me	Cl		1.75	2.10	1.23	1.23	5.80	2.13	—		8.3	8.3	~1
Phb	Me	Br		1.73	2.01	1.24	1.21	5.94	2.32	—	11±3%	8.5	8.0	1.4
Me	Cl	Me	(E)-cis	(1.64)	(1.73)	(1.25)	(1.22)	5.83	—	2.09		(7.5)	(7.5)	1.4
Phb	Cl	Me		(1.67)	(1.71)	(1.23)	(1.20)	5.83	—	2.09				1.4
H	Br	Me		1.71	1.84	1.30	1.25	6.01	—	2.28	3±2%	8.6	8.1	1.4
Phb	Br	Me		(1.71)	(1.73)	1.23	1.19	6.04	—	2.24	3±4%			1.4
Me	Me	Me	cis	1.56	1.76	1.20	1.20	5.34	1.74	1.66	7±2%	8.8	8.1	1.3
Me	Cl	Cl	cis	1.76	1.97	1.26	1.26	6.26	—	—		8.7	8.6	—

^a For the structure and numbering, see Fig. 1.^b Nuclear Overhauser effect between 1'-H and either C-3' or C-4'.

above (see Table II). The 3-H ring proton of the (Z)-isomers is found in a lower field than those of the (E)-isomers in both the *cis* and *trans* isomers and, furthermore, with respect to the configuration on the cyclopropane ring, the 3-H ring proton of the *trans* isomers appears in a lower field than those of the *cis* isomers: the order of magnitude in the chemical shifts of the 3-H proton is as follows: (Z)-*trans* > (Z)-*cis* ≥ (E)-*trans* > (E)-*cis* = 2.15 ~ 2.29 > 2.01 ~ 2.10 ≥ 1.96 ~ 2.04 > 1.71 ~ 1.84. This observation may be primarily caused by the induced anisotropic and steric effects of the halogen atom. This atom is relatively close to the 3-H ring proton in the Z-configuration within the extent of the preferred conformations of the vinyl group as discussed above, and secondly by the effect that the 3-H proton in the *trans* isomer receives the anisotropic

effects of the carboxyl group laying on the same side.

EXPERIMENTAL

All melting and boiling points were uncorrected. IR spectra were measured on a JASCO IR-A2 Spectrometer. NMR spectra were obtained in Varian High Resolution NMR Spectrometer Model A-60, EM-390 and HA-100 or a Hitachi R-24 High Resolution NMR Spectrometer using tetramethylsilane as an internal standard. Chemical shifts were expressed in ppm. Analytical determination by glc was performed on a Gaschro Kogyo Inc. KOR-70 model gaschromatograph. Mass spectra were recorded on Japan Electron Optics Lab. JMS-01SG Spectrometer.

Ethyl 3,3-dimethyl-4,6,6-trichloroheptanoate (2). The reaction conditions and results are given in Table I. A typical experimental procedure (run 2) was as follows: A mixture of the olefin 1 (46.7 g, 0.3 mol), 1,1,1-trichloroethane (120 g, 0.9 mol), iron (II) chloride tetrahydrate

(6.0 g 0.03 mol) and hexamethylphosphoramide (HMPA) (29.3 g, 0.16 mol) was placed in a sealed tube of stainless steel, and the air was purged by argon. After being heated for 18 hr at 125~130°C, the mixture was poured into 1% hydrochloric acid and extracted with ethyl acetate. The extracts were dried over MgSO_4 and the solvent was then evaporated *in vacuo* to give an oily residue, which was distilled to afford 60.8 g of **2** in a 70% yield, bp 97~100°C/0.2 mmHg; IR $\nu_{\text{max}}^{\text{film}}$ cm^{-1} : 1730 (C=O); NMR (CCl_4) δ : 1.12 (3H, s, CH_3), 1.20 (3H, s, CH_3), 1.25 (3H, t, OCH_2CH_3), 2.25 (1H, d, $J=15.5$ Hz, $-\text{CHHCO}_2$), 2.25 (3H, s, CH_3), 2.52 (1H, dd, $J=7.5$ and 15.5 Hz, $-\text{CClH}-\text{CHH}$), 2.53 (1H, d, $J=15.5$ Hz, $-\text{CHHCO}_2$), 3.00 (1H, dd, $J=2.0$ and 15.5 Hz, $-\text{CClH}-\text{CHH}$), 4.10 (2H, q, OCH_2CH_3), 4.30 (1H, dd, $J=2.0$ and 7.5 Hz, $-\text{CHCl}-$); MS m/z : 247, 245, 243 (^{35}Cl M-OEt), 216, 129.

Ethyl trans-3-(2,2-dichloropropyl)-2,2-dimethylcyclopropanecarboxylate (3) and ethyl cis-3-(2,2-dichloropropyl)-2,2-dimethylcyclopropanecarboxylate (4). To a solution of **2** (10.9 g, 0.038 mol) in 150 ml of benzene was slowly added dropwise a solution of sodium *tert*-pentoxide (prepared from 5.0 g of 55% sodium hydride and 20 g of *tert*-pentyl alcohol) in 100 ml of benzene at 10~20°C during 1 hr, and the mixture stirred at room temperature for 1 hr. The reaction mixture was diluted with ice-cooled water and extracted with ether. The extracts were washed with water and dried over Na_2SO_4 . Evaporation of the solvent *in vacuo* gave a crude mixture of **3** and **4**, which were separated by column chromatography on silicagel (hexane : benzene = 75 : 25) to afford 5.43 g of **3**, 0.85 g of **4** and 1.92 g of a mixture of **3** and **4** (in an 86% combined yield).

3: IR $\nu_{\text{max}}^{\text{film}}$ cm^{-1} : 1720, 1180, 1170; NMR (CDCl_3) δ : 1.18 (3H, s, CH_3), 1.27 (3H, s, CH_3), 1.27 (3H, t, $J=7.5$ Hz, OCH_2CH_3), 1.35 (1H, d, $J=5.0$ Hz, CHCHCO_2), 1.68 (1H, ddd, $J=5.0$, 6.5 and 7.0 Hz, CH_2CHCH), 2.17 (3H, s, CH_3), 2.24 (1H, dd, $J=6.5$ and 15 Hz, $-\text{CHH}-$), 2.72 (1H, dd, $J=7.0$ and 15 Hz, $-\text{CHH}-$), 4.24 (2H, q, $J=7.5$ Hz, OCH_2CH_3); MS m/z : 252 (^{35}Cl M⁺), 217, 175, 141, 103.

4: IR $\nu_{\text{max}}^{\text{film}}$ cm^{-1} : 1720, 1180, 1130; NMR (CDCl_3) δ : 1.22 (6H, s, $2 \times \text{CH}_3$), 1.24 (3H, t, $J=7.5$ Hz, OCH_2CH_3), 1.30~1.75 (1H, m, $-\text{CHCHCO}_2$), 1.48 (1H, dd, $J=1.5$ and 14.3 Hz, $-\text{CHCO}_2$), 2.15 (3H, s, CH_3), 2.48 (1H, ddd, $J=1.5$, 5.0 and 19.5 Hz, $-\text{CHH}-$), 2.68 (1H, dd, $J=5.5$ and 19.5 Hz, $-\text{CHH}-$), 4.09 (2H, q, $J=7.5$ Hz, OCH_2CH_3); MS m/z : 252 (^{35}Cl M⁺), 217, 175, 141, 103.

Dehydrochlorination of ethyl trans-3-(2,2-dichloropropyl)-2,2-dimethylcyclopropanecarboxylate (3). A mixture of 23.7 g (0.094 mol) of **3** and 28.5 g (0.187 mol) of DBU was heated at 85°C for 3.5 hr. After cooling, water was added to the mixture, which was then acidified with 10% hydrochloric acid and extracted with ether. The extracts were washed with water, dried over Na_2SO_4 and evaporated *in vacuo* to give a residue, which was subjected

to distillation to afford 15.85 g of a mixture of **5a**, **6a** and **7a** (**5a**/**6a**/**7a** = 3/6/1 by glc: silicon OV-17, 105°C) in a 78% yield, bp 86~89°C/0.3 mmHg. The mixture of **5a**, **6a**, and **7a**: IR $\nu_{\text{max}}^{\text{film}}$ cm^{-1} : 1725, 1655, 1170; NMR (CCl_4) δ : 1.10~1.50 (7H, m, $2 \times \text{CH}_3$ and $-\text{CHCO}_2$), 1.27 (3H, t, $J=7.5$ Hz, OCH_2CH_3), 1.80~2.50 (1H, m, $=\text{CH}-\text{CH}-$), 2.13 (3H, m, CH_3), 4.11 (2H, q, $J=7.5$ Hz, OCH_2CH_3), 5.10~5.45 (1H, m, $=\text{CH}-$); MS m/z : 216 (^{35}Cl M⁺), 181, 153, 143, 107.

Dehydrochlorination of ethyl cis-3-(2,2-dichloropropyl)-2,2-dimethylcyclopropanecarboxylate (4). A mixture of 506 mg (2 mmol) of **4** and 320 mg (8 mmol) of sodium hydroxide in 5 ml of methanol was heated under reflux for 5.5 hr. After cooling, 5 ml of 1 N sodium hydroxide was added to the reaction mixture and the solution was extracted with ether. The aqueous layer was acidified with 1 N hydrochloric acid and extracted with ether. The extracts were dried over Na_2SO_4 and evaporated *in vacuo* to give 355 mg of a mixture of **8b** and **9b** in an 82% yield. A part of the mixture was esterified with diazomethane and glc analysis of the resulting methyl ester (glc: silicone OV-17, 105°C) revealed it to be a mixture of **8b** and **9b** with the ratio of 40 : 60, respectively.

The mixture of **8b** and **9b**: IR $\nu_{\text{max}}^{\text{film}}$ cm^{-1} : 1680, 1230; NMR (CDCl_3) δ : 1.18 (6H, s, $2 \times \text{CH}_3$), 1.45~2.40 (2H, m, $-\text{CHCH}-$), 2.06 (3H, m, CH_3), 5.65~5.97 (1H, m, $-\text{CH}=$), 11.40 (1H, broad s, COOH); MS m/z : 188 (^{35}Cl M⁺), 153, 143, 117, 107.

(Z)-trans-3-(2-chloro-1-propenyl)-2,2-dimethylcyclopropanecarboxylic acid (6b). A mixture of **5a** and **6a** (15.85 g, 0.073 mol) in 50 ml of methanol and sodium hydroxide solution (prepared from 3.64 g of sodium hydroxide and 25 ml of water) was refluxed for 2.5 hr. After cooling, the methanol was evaporated *in vacuo*, water was added to the residue and it was then extracted with ether. The aqueous layer was acidified with dil. hydrochloric acid and extracted with ether. The extracts were washed with water and dried over Na_2SO_4 . Evaporation of the solvent *in vacuo* afforded 13.5 g of the crude acid, which was recrystallized in 25 ml of hexane to give 3.20 g of the (*Z*)-*trans* acid **6b** mp 89~92°C. IR $\nu_{\text{max}}^{\text{Nujol}}$ cm^{-1} : 1680, 1240, 700; NMR: see Table II; MS m/z : 188 (^{35}Cl M⁺), 153, 143, 107; *Anal.* Calcd. for $\text{C}_9\text{H}_{13}\text{ClO}_2$: C, 57.30; H, 6.94; Cl, 18.79%. Found: C, 57.11; H, 6.89; Cl, 18.91%.

(Z)-cis-3-(2-chloro-1-propenyl)-2,2-dimethylcyclopropanecarboxylic acid (9b). In a similar manner to **6b**, the mixture of **8a** and **9a** was hydrolyzed by sodium hydroxide in methanol followed by recrystallization from hexane to give (*Z*)-*cis* acid (**9b**) mp 105~112°C. IR $\nu_{\text{max}}^{\text{Nujol}}$ cm^{-1} : 1680, 1230; NMR (CDCl_3) δ : 1.27 (6H, s, $2 \times \text{CH}_3$), 1.73 (1H, d, $J=4.0$ Hz, $-\text{CHCO}_2$), 2.18 (3H, m, CH_3), 2.03~2.38 (1H, m, $=\text{CHCH}-$), 5.80 (1H, broad d, $J=8.5$ Hz, $-\text{CH}=$), 11.77 (1H, broad, COOH);

MS m/z : 188 ($^{35}\text{Cl M}^+$), 153, 143, 117, 107; *Anal.* Calcd. for $\text{C}_9\text{H}_{13}\text{ClO}_2$: C, 57.30; H, 6.94; Cl, 18.79%. Found: C, 57.45; H, 7.01; Cl, 18.63%.

m-Phenoxybenzyl (Z)-trans-3-(2-chloro-1-propenyl)-2,2-dimethylcyclopropanecarboxylate (**6d**). To a solution of **6b** (377 mg, 2 mmol) in 2 ml of benzene was added 357 mg of thionyl chloride and the solution was refluxed for 30 min. After removing the benzene and excess thionyl chloride *in vacuo*, the resulting acid chloride and *m*-phenoxybenzyl alcohol (440 mg, 2.2 mmol) were dissolved in 2 ml of benzene. To the solution was added 347 mg of pyridine in 2 ml of benzene at 0°C and the mixture stirred overnight at room temperature. After the addition of ether, the resulting solution was washed with water and dried over Na_2SO_4 . After removing the solvent, the residue was purified by column chromatography on silicagel (hexane : benzene = 1 : 1) to give 532 mg of **6d** in a 71% yield. IR $\nu_{\text{max}}^{\text{film}} \text{cm}^{-1}$: 1735, 1170; NMR (CCl_4) δ : 1.12 (3H, s, CH_3), 1.24 (3H, s, CH_3), 1.47 (1H, d, $J=5.0$ Hz, $-\text{CHCO}_2$), 2.02 (3H, m, CH_3), 2.10~2.40 (1H, m, $=\text{CHCH}-$), 5.08 (2H, s, $-\text{OCH}_2$), 5.15 (1H, broad d, $J=8.0$ Hz, $=\text{CH}-$), 6.70~7.50 (9H, m, phenyl H); MS m/z : 370 ($^{35}\text{Cl M}^+$), 335, 183, 143, 107.

m-Phenoxybenzyl esters of 3-(2-chloro-1-propenyl)-2,2-dimethylcyclopropanecarboxylate (**5d**, **8d** and **9d**). In a similar manner to **6d**, a mixture of (*E*)- and (*Z*)-cis esters (**8d** and **9d**) and (*E*)- and (*Z*)-trans esters (**5d** and **6d**) was prepared from the corresponding acids in 61% and 89% yields, respectively. Each mixture was separated into the (*E*)- and (*Z*)-isomers by HPLC (Waters, μ Porasil, hexane : ether = 1000 : 1).

5d: IR $\nu_{\text{max}}^{\text{film}} \text{cm}^{-1}$: 1730; NMR (CCl_4) δ : 1.17 (3H, s, CH_3), 1.23 (3H, s, CH_3), 1.48 (1H, d, $J=5.0$ Hz, $-\text{CHCO}_2$), 2.0~2.3 (1H, m, $=\text{CHCH}-$), 2.12 (3H, m, CH_3), 5.10 (2H, s, OCH_2), 5.35 (1H, broad d, $J=8.0$ Hz, $-\text{CH}=\text{}$), 6.80~7.55 (9H, m, phenyl H); MS m/z : 370 ($^{35}\text{Cl M}^+$), 335, 183, 143, 107.

8d: IR $\nu_{\text{max}}^{\text{film}} \text{cm}^{-1}$: 1730, 1140, 700; NMR: see Table II; MS m/z : 370 ($^{35}\text{Cl M}^+$), 335, 183, 143.

9d: IR $\nu_{\text{max}}^{\text{film}} \text{cm}^{-1}$: 1730, 1590, 1140, 700; NMR: see Table II; MS m/z : 370 ($^{35}\text{Cl M}^+$), 335, 183, 143.

Photoisomerization of a mixture of ethyl (E)-trans-3-(2-chloro-1-propenyl)-2,2-dimethylcyclopropanecarboxylate (5a) and ethyl (Z)-trans-3-(2-chloro-1-propenyl)-2,2-dimethylcyclopropanecarboxylate (6a). A solution of the mixture of **5a** and **6a** (217 mg, 1 mmol) and acetophenone (240 mg, 2 mmol) in 10 ml of benzene was placed in a conventional glass vessel under cooling with ice-cooled water. The mixture was irradiated with a high pressure mercury lamp for 4 hr under a nitrogen atmosphere. After removing the solvent, the residue was purified by column chromatography on silicagel (hexane : benzene = 3 : 1) to afford 162 mg of colorless oil, which was separated by preparative TLC on silicagel (hexane : benzene = 1 : 1) to

give 19 mg of **8a** and 73 mg of a mixture of **5a**, **6a** and **9a** consisting of (**5a** + **6a**) : **9a** = 85 : 15.

8a: NMR: see Table II.

Isomerization of a mixture of (E)- and (Z)-cis-3-(2-chloro-1-propenyl)-2,2-dimethylcyclopropanecarboxylic acids (8b and 9b). A solution of the acids (**8b** : **9b** = 17 : 83, 0.20 g, 1.16 mmol), *p*-toluenesulfonic acid (0.02 g, 0.116 mmol) and acetic anhydride (0.068 g, 0.67 mmol) in 2 ml of xylene was refluxed for 2 hr. After cooling, the solvent was evaporated *in vacuo* and 2 ml of 1 N sodium hydroxide solution and 6 ml of methanol was added to the residue. After heating for 1 hr at 60~80°C, the methanol was evaporated *in vacuo*, 2 ml of 1 N sodium hydroxide was added to the residue which was then extracted with ether. The aqueous solution was acidified with 1 N hydrochloric acid solution and extracted with ether. The extracts were dried over Na_2SO_4 and evaporated *in vacuo* to give 0.18 g of the mixture of **5b**, **6b** and **9b** in a 90% yield. A part of the mixture was esterified with diazomethane and glc analysis (PEG 20 M, 140°C) revealed a mixture of **5b**, **6b** and **9b** with the ratio of 17 : 69 : 14, respectively.

Ethyl 3,3-dimethyl-4,6,6-tribromoheptanoate (11). A mixture of the olefin **1** (1.56 g, 10 mmol), 1,1,1-tribromoethane (8.00 g, 30 mmol) and $\text{RuCl}_2[(\text{C}_6\text{H}_5)_3\text{P}]_3$ (96 mg, 0.1 mmol, 1 mol%) was placed in a sealed tube of stainless steel and the mixture was heated at 100~105°C for 15 hr. After the filtration of the precipitates, the filtrate was concentrated *in vacuo* and the residue was purified by column chromatography on silicagel to give 270 mg of **11** in a 6.4% yield. NMR (CCl_4) δ : 1.09 (3H, s, CH_3), 1.18 (3H, s, CH_3), 1.18 (3H, t, $J=7.0$ Hz, OCH_2CH_3), 2.16 (1H, d, $J=15$ Hz, $-\text{CHHCO}_2$), 2.65 (1H, d, $J=15$ Hz, $-\text{CHHCO}_2$), 2.61 (3H, s, CH_3), 2.83 (1H, dd, $J=7.5$ and 17 Hz, $-\text{CHHCHBr}_2$), 3.37 (1H, dd, $J=2.0$ and 17 Hz, $-\text{CHHCHBr}_2$), 4.05 (2H, q, $J=7.0$ Hz, OCH_2CH_3), 4.33 (1H, dd, $J=2.0$ and 7.5 Hz, $-\text{CHBr}$).

Methyl (E)-cis-3-(2-bromo-1-propenyl)-2,2-dimethylcyclopropanecarboxylate (13c) and methyl (Z)-cis-3-(2-bromo-1-propenyl)-2,2-dimethylcyclopropanecarboxylate (14c). To a stirred suspension of 1,1-dibromoethylphosphonium bromide (21.3 g, 0.04 mol) in 40 ml of THF was added dropwise 24.8 ml (0.04 mol) of butyl lithium (a 1.62 M solution in hexane) at -45~-40°C, stirring being continued at -40°C for 20 min. The solution of **12c** (4.82 g, 0.03 mol) in 15 ml of THF was added dropwise to the ylide solution at -45°C. After being stirred at -45°C for 20 min, the mixture was quenched with saturated aqueous ammonium chloride and extracted with ether. The extracts were washed with water and dried over Na_2SO_4 . After removing the solvent, the residue was purified by column chromatography on silicagel (hexane : benzene = 1 : 1) to give 5.67 g of a mixture of **13c** and **14c** in a 75% yield. The mixture of **13c** and **14c**: NMR (CDCl_3) δ : 1.28 (3H, s, CH_3), 1.30

(3H, s, CH₃), 1.80~1.97 (2H, m, -CHCH-), 2.37 (3H, s, CH₃), 3.76 (3H, s, OCH₃), 6.03~6.35 (1H, m, =CH-).

m-Phenoxybenzyl esters of 3-(2-bromo-1-propenyl)-2,2-dimethylcyclopropanecarboxylate (**13d**, **14d**, **16d** and **17d**). In the similar manner to **13c** and **14c**, a mixture of **13d** and **14d** and a mixture of **16d** and **17d** were prepared from the corresponding aldehydes of the *m*-phenoxybenzyl ester in 37.7% and 62% yields, respectively. The (*E*)- and (*Z*)-isomers was separated from the mixture by column chromatography on silicagel.

13d: IR $\nu_{\text{max}}^{\text{film}}$ cm⁻¹: 1730, 1585, 1140, 690; NMR: see Table II; MS *m/z*: 414 (⁷⁹Br M⁺), 335, 235, 189, 187, 183.

14d: IR $\nu_{\text{max}}^{\text{film}}$ cm⁻¹: 1730, 1585, 1135, 690; NMR: see Table II; MS *m/z*: 414 (⁷⁹Br M⁺), 335, 235, 189, 187, 183.

16d: IR $\nu_{\text{max}}^{\text{film}}$ cm⁻¹: 1720, 1585; NMR (CDCl₃) δ : 1.17 (3H, s, CH₃), 1.25 (3H, s, CH₃), 1.57 (1H, d, *J* = 5.0 Hz, -CHCO₂), 2.05 (1H, dd, *J* = 5.0 and 9.0 Hz, -CHCHCO₂), 2.29 (3H, m, CH₃), 5.11 (2H, s, OCH₂), 5.59 (1H, broad d, *J* = 9.0 Hz, -CH =), 6.82~7.48 (9H, m, phenyl H); MS *m/z*: 414 (⁷⁹Br M⁺) 335, 325, 189, 187, 183.

17d: IR $\nu_{\text{max}}^{\text{film}}$ cm⁻¹: 1720, 1585; NMR (CDCl₃) δ : 1.16 (3H, s, CH₃), 1.28 (3H, s, CH₃), 1.57 (1H, d, *J* = 5.0 Hz, -CHCO₂), 2.16~2.40 (1H, m, -CHCHCO₂), 2.29 (3H, m, CH₃), 5.11 (2H, s, OCH₂), 5.43 (1H, broad d, *J* = 7.0 Hz, -CH =), 6.86~7.49 (9H, m, phenyl H); MS *m/z* 414 (⁷⁹Br M⁺), 335, 235, 189, 187, 183, 108.

(*E*)-*cis*-3-(2-Bromo-1-propenyl)-2,2-dimethylcyclopropanecarboxylic acid (**13b**). A solution of the acid (2.0 g of a mixture of **13c** and **14c**) and sodium hydroxide (420 mg) in 35 ml of methanol and 15 ml of water was stirred for 3.5 hr at 55°C. After cooling, the methanol was evaporated *in vacuo*, water was added to the residue and the solution extracted with ether. The aqueous layer was acidified with dil. hydrochloric acid and extracted with ether. The extracts were washed with water and dried over Na₂SO₄. Evaporation of the solvent afforded 1.67 g of the crude acids, which were recrystallized from hexane to give 700 mg of the (*E*)-*cis* acid **13b**, mp 101~104°C. IR $\nu_{\text{max}}^{\text{Nujol}}$ cm⁻¹: 1675, 1240; NMR: see Table II; Anal. Calcd. for C₉H₁₃BrO₂: C, 46.37; H, 5.62; Br, 34.28%. Found: C, 46.55; H, 5.57; Br, 34.01%.

(*Z*)-*trans*-3-(2-Bromo-1-propenyl)-2,2-dimethylcyclopropanecarboxylic acid (**17b**). In a similar manner to **13b**, a mixture of **16c** and **17c** was hydrolyzed by sodium hydroxide in methanol followed by recrystallization from hexane to give (*Z*)-*trans* acid (**17b**), mp 90~99°C. NMR: see Table II; Anal. Calcd. for C₉H₁₃BrO₂: C, 46.37; H, 5.62; Br, 34.28%. Found: C, 46.73; H, 5.66; Br, 33.91%.

Transesterification of the mixture of 13c and 14c with m-phenoxybenzyl alcohol. A solution of the mixture of **13c**

and **14c** (1.0 g, 4.05 mmol), *m*-phenoxybenzyl alcohol (1.3 g, 6.5 mmol) and a catalytic amount of lithium amide in 50 ml of toluene was refluxed for 3 hr under continuous removal of methanol as a toluene azeotrope. After removing the solvent, the residue was separated by column chromatography on silicagel (hexane : ethyl acetate = 20:1) to give 1.44 g of a mixture of **13d** and **14d**. This mixture of **13d** and **14d** was separated by preparative TLC on silicagel (hexane : ethyl acetate = 20:1) to give 0.95 g of **13d** and 0.25 g of **14d**.

m-Phenoxybenzyl *trans*-3-formyl-2,2-dimethylcyclopropanecarboxylate (**15d**). To a solution of *trans* phenothrin (20 g, 5.7 nmol) in 7.2 ml of water and 30 ml of dioxane was added 2 ml of a 1% aqueous solution of osmium tetroxide at room temperature. After stirring for 5 min, sodium periodate (3.65 g, 17 mmol) was added to the mixture which was then stirred at room temperature for 39 hr. The resulting precipitates were removed by filtration and the filtrate was extracted with ether. The extracts were washed with water and dried over Na₂SO₄. After removing the solvent, the residue was purified by column chromatography on silicagel to give 1.37 g of **15d** in a 79% yield. NMR (CDCl₃) δ : 1.20 (3H, s, CH₃), 1.23 (3H, s, CH₃), 2.38~2.47 (2H, m, -CHCH-), 5.05 (2H, d, *J* = 4.0 Hz, -CH₂), 6.80~7.50 (9H, m, phenyl H), 9.61 (1H, m, -CHO).

m-Phenoxybenzyl *cis*-3-formyl-2,2-dimethylcyclopropanecarboxylate (**12d**). In a similar manner to **15d**, *m*-phenoxybenzyl *cis*-3-formyl-2,2-dimethylcyclopropanecarboxylates (**12d**) was prepared from the corresponding chrysanthemate in a 32.7% yield. NMR (CDCl₃) δ : 1.05 (3H, s, CH₃), 1.32 (3H, s, CH₃), 1.66 (1H, dd, *J* = 6.5 and 8.0 Hz, -CHCHO), 2.00 (1H, d, *J* = 8.0 Hz, -CHCO₂), 5.00 (2H, s, OCH₂), 6.76~7.48 (9H, m, phenyl H), 9.76 (1H, d, *J* = 6.5 Hz, CHO).

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