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Transformation of 3-(2,2-Dichloroethenyl)-2,2-dimethylcyclopropanecarboxylates to the Corresponding 2,2-Dibromoethenyl Analogs by Halogen Exchange Reaction[1)]

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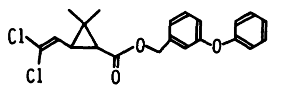
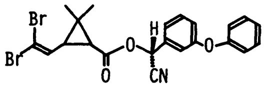
The title transformation is effected with aluminium tribromide or related reagents in over 80% yields without cis-trans isomerization or epimerization. Efficient removal of hydrogen bromide is essential for optimum yields of the desired products. Use of boron tribromide instead of aluminium tribromide results in opening of the cyclopropane ring with no halogen exchange.

A new artificial pyrethroid having 2,2-dichloroethenyl substituent, i.e., permethrin (**1**),[2)] is now one of the common agricultural insecticides thanks to its moderate stability and high insecticidal activity. Its dibromoethenyl analog, decamethrin (**2**), is found by Elliott et al.[3)] and revealed to be more than ten times as active as permethrin.



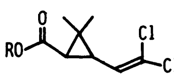
permethrin (**1**)
(cis-, trans- and
racemic mixture)



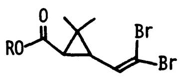
decamethrin (**2**)
(ester of (1*R*)-cis acid)

To the synthesis of permethrin, we developed a convenient process, which involved the addition of carbon tetrachloride to 3,3-dimethyl-4-pentenoates (**3**) and successive dehydrochlorination and cyclization of 4,6,6,6-tetrachloro-3,3-dimethylhexanoates (**4**) with a base to afford 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylates (**5**).[4)]

In the case of decamethrin synthesis, the method was applied with less synthetic value because of the following drawbacks: (a) The addition of carbon tetrabromide to **3** was relatively inefficient; (b) Trans-rich 3-(2,2-dibromoethenyl)-2,2-dimethylcyclopropanecarboxylates (**6**) was usually produced upon base-treatment of the resulting adduct.[4)]



5



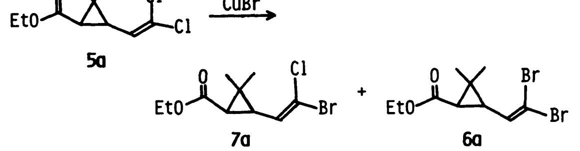
6

a: R=Et, b: R=Me, c: R=H

The processes developed so far by other groups also involve such serious disadvantages as low product yields, high cost and/or tedious operations.[3,5)]

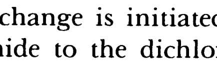
This paper details the conversion of dichloroethenyl compounds **5** to the corresponding dibromoethenyl analogs **6** by halogen exchange which provides a convenient route to decamethrin.

Exchange of the halogen of haloethenes has been usually performed with copper(I) halides in dipolar aprotic solvents.[6)] We first attempted the reaction of **5a** with copper(I) bromide under various conditions and obtained a mixture of dichloro-, bromochloro-, and dibromoethenylcyclopropanecarboxylates (**5a**, **7a**, and **6a**, respectively). For example, treatment of **5a** with copper(I) bromide (8 equiv) in DMF at 150 °C for 8 h afforded a mixture of **5a** (77%), **7a** (16%), and **6a** (1%). The prolonged treatment usually induced the decomposition of the products and the total recovery of **5a**, **6a**, and **7a** diminished. Use of a large excess of copper(I) bromide gave no significant change in product distribution.



Aluminium tribromide and boron tribromide are also capable of halogen exchange.[7)] They are active for the halogen exchange of relatively stable compounds such as simple alkyl halides,[8)] gem-polyhalogenated compounds,[9)] bridgehead-halogenated bicyclic compounds,[10)] and a few haloethenes.[11)]

We found aluminium tribromide did promote the halogen exchange of **5a** without affecting the ester group or cyclopropane ring as follows: Treatment of **5a** with commercial aluminium tribromide in 1,2-dibromoethane under ice-water cooling afforded **6a** (area % on GLPC=88%) and **7a** (5%) along with a by-product (6%). The structure of this by-product was assigned to 2,2,2-tibromoethyl compound **8a** by the GLPC-MS data and by its conversion to **6a** with DBU. A 76% yield of **6a** with 95% purity was attained by transforming the concomitant **8a** into **6a**.



8a

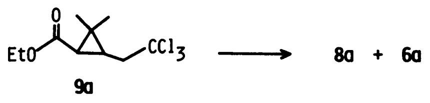
The formation of **8a** suggests the possibility that the halogen exchange is initiated by the addition of hydrogen bromide to the dichloroethenyl moiety of **5a**.[12)] This hypothesis prompted us to study the halogen exchange of 2,2,2-trichloroethyl compound **9a** with aluminium tribromide. The reaction in fact pro-

Table 1. Direct Conversion of **9a** and **5a** to **6a** Using HBr Scavenger

Substrate	HBr scavenger	Time h	Yield (GLPC)/% **6a**	**8a**	**7a**
9a	Al metal	7.5	23.4	15.5	0.8
9a	Pyridine	4.5	49.3	33.1	4.7
9a	Na_2CO_3	7.0	56.7	26.5	4.1
9a	Argon[a)]	6.0	82.9	11.8	3.7
9a	Argon, red. press.[b)]	3.0	95.6	4.2	—
5a	Argon, red. press.[b)]	4.0	91.0	1.8	1.7

a) Argon=The reaction mixture was bubbled with argon gas under ice-water cooling. b) Argon, red. press.=The reaction mixture was bubbled with argon gas under reduced pressure (≈20 mmHg) under ice-water cooling.

ceeded smoothly in dibromomethane, and tribromoethyl compound **8a** was produced in 62% yield accompanied by ca. 30% of dibromoethenyl compound **6a**.



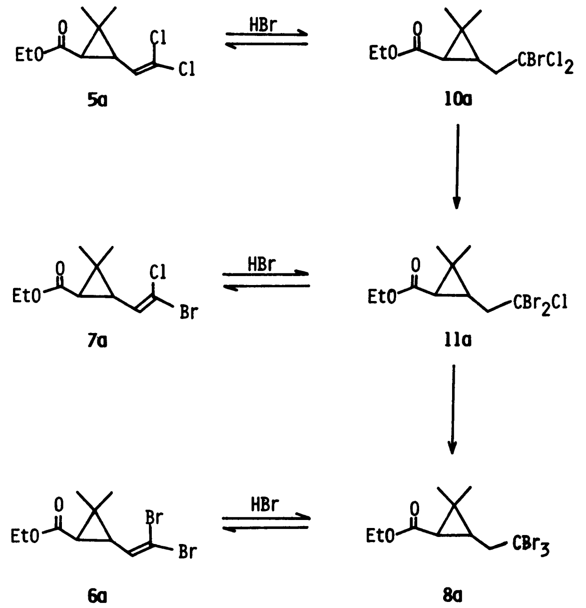
The formation of **6a** suggests that the aluminium trihalides promotes also the dehydrobromination of the tribromoethyl moiety.

Therefore, we then studied the conversion of **9a** into **6a** and the complete transformation of **5a** into **6a**. Such hydrogen bromide scavenger as aluminium metal, pyridine or sodium carbonate turned out ineffective in the transformation of **9a** into **6a** (Table 1). In order to purge the hydrogen bromide, the reaction mixture was bubbled by an argon gas with promising results. Finally, argon bubbling under reduced pressure was found to be most effective, and the contaminating **8a** was reduced to below 5% (Table 1). By using this technique, **9a** and **5a** were successfully transformed into **6a** as shown in Table 1.

The reagent generated from aluminium metal and 1,2-dibromoethane (or bromine, or hydrogen bromide) was found also effective for the transformation of **5a** to **6a**. Furthermore, aluminium trichloride could be used instead of aluminium tribromide when hydrogen bromide was introduced during the reaction. In practical view point, the aluminium metal-hydrogen bromide reagent (91% yield, 95% purity) and aluminium trichloride-hydrogen bromide reagent (92% yield, 91% purity) were most useful. Other metal bromides, e.g., $ZnBr_2$, $FeBr_3$, $CuBr_2$, $BiBr_3$, $SbBr_3$, $HgBr_2$, $TiBr_4$, were almost ineffective for this halogen exchange.

Brominated hydrocarbon, e.g., dibromomethane, or 1,2-dibromoethane, was the most appropriate solvent and the use of aromatic halides and carbon disulfide gave comparable results. In dichloromethane, the halogen exchange was not so effective as in the case of dibromomethane. The optimum amount of the aluminium reagent was found to be ca. 1.5 molar equivalents of the substrate in view of the product yield and the purity. The halogen exchange did not occur with less than one molar equivalent of the reagent. The product yield decreased with a large excess reagent.

These findings may suggest the reaction mechanism for the halogen exchange reaction as illustrated in Scheme 1: (1) Addition of hydrogen bromide to the dichloroethenyl moiety.[13)] (2) Halogen exchange of the trihaloethyl intermediates (**10a**, **11a**, and **8a**). (3) Dehydrobromination of these intermediates. The aluminium reagents should have played an important role in the above every step.



Scheme 1.

The chlorine-bromine exchange reaction is applicable as well to the methyl ester **5b** or free acid **5c**. The yields of the corresponding dibromoethenyl compound **6b** or **6c** were also satisfactory. The exchange reaction of the free acid **5c** proceeded faster than that of the corresponding esters. Actually, the halogen exchange of **5c** almost finished when the addition of the substrate to aluminium tribromide was completed. In this acid case, the formation of tribromoethyl acid **8c** was remarkable as compared with the ester cases (**6c**/**8c**=1/2). The rapid halogen exchange and the presence of a larger amount of **8c** is attributed to the hydrogen bromide generated by the initial contact of the starting acid **5c** with the aluminium reagent. Efficient removal of hydrogen bromide from the reaction mixture by argon bubbling was, therefore, necessary for optimum yield of dibromoethenyl acid **6c** (90—95%).

In order to apply this halogen exchange to the preparation of the acid part of decamethrin, it is essential that cis-trans isomerization or epimerization should not take place during the reaction.

Table 2. Stereochemistry in Transformation of **5** to **6**

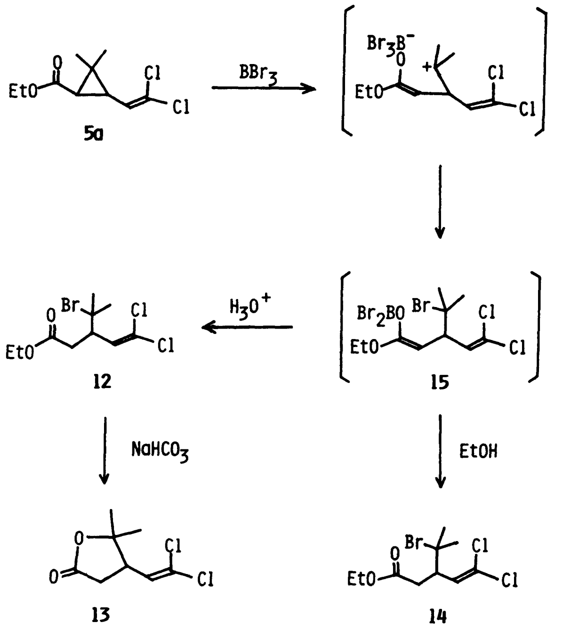
5 (cis/trans)	Reagent	**6** Yield/%	cis/trans	Purity/%[a]
5a (77/23)	Al-HBr	92	77/23	95
5b (99/1)	Al-HBr	90	99/1	92
5c (0/100)	$AlBr_3$	93	0/100	96
5c (100/0)	$AlBr_3$	94	100/0	96
5c (0/100)[b]	$AlBr_3$	93	0/100[c]	96

a) Based on GLPC area %. b) $[\alpha]_D=-36.3°$ ($CHCl_3$). c) $[\alpha]_D=-37.2°$ ($CHCl_3$).

The halogen exchange upon the dichloroethenyl compounds **5a**—**c** of various cis/trans ratio showed complete preservation of the original stereochemistry as shown in Table 2.

For example, 100% *trans*-dibromoethenyl acid **6c** was obtained by the treatment of 100% *trans*-dichloroethenyl acid **5c** with aluminium tribromide. Similarly, 100% *cis*-**5c** was stereospecifically converted into 100% *cis*-**6c** in an excellent yield. The retention of the stereochemistry was also verified in the last example. Acid *trans*-**5c** with ca. 98% optical purity was transformed into **6c** having over 90% optical purity.[14]

Boron tribromide is also known to be capable of halogen exchange.[11] When dichloroethenyl compound **5a** was treated with boron tribromide in dibromomethane at room temperature, **5a** disappeared completely after stirring overnight. Acidification of the reaction mixture followed by usual work-up afforded only a carboxylic acid which was readily transformed into a neutral compound by treating with aqueous sodium hydrogencarbonate. The former carboxylic acid was assigned to ring-opened acid **12** and the neutral compound to **13** (Scheme 2). The yields of the two products were 65 and 63%, respectively, based on **5a**. When the reaction mixture was quenched with dry ethanol, the ester **14** was obtained in 89% yield. Scheme 2 shows possible routes to these products. The coordination of boron tribromide to the ester carbonyl followed by the ring opening and the transfer of bromide ion to the cationic carbon produces intermediary ethenyl borate **15**.[18] Hydrolysis or ethanolysis of **15** affords **12** or **14** as the final product. No halogen exchange was observed during this reaction. The stronger Lewis acidity of boron tribromide than aluminium tribromide would account for the observed different reactivity between them.



Scheme 2.

Experimental

General. All the melting points and boiling points are uncorrected. IR spectra were recoreded on a Hitachi EPI-G3 grating spectrophotometer. ^1H NMR spectra were measured with Varian HA-100 spectrometer and Hitach-Perkin-Elmer R-20B using TMS as an internal standard. Mass spectra were recoreded on Hitachi RMU-6E mass spectrometer (70 eV). Analytical determinations by GLPC were performed on a Hitachi 163 gas chromatograph (5 mm o.d.×1 m, 2% EGA on Uniport B or diasolid ZS).

Attempted Halogen Exchange of Ethyl 3-(2,2-Dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate (5a) with CuBr. A solution (DMF or DMSO) of **5a** (0.47 g, 2.0 mmol) was added to a mixture of CuBr (16—40 mmol) in the same solvent (total 5 ml). The resulting mixture was heated at 130—150 °C for 8—55.5 h under an argon atmosphere. The composition of the reaction mixture was checked by GLPC at intervals.

Halogen Exchange of 5a with $AlBr_3$ in 1,2-Dibromoethane and Succesive Dehydrobromination with DBU. A solution of $AlBr_3$ (Kishida Kagaku, GR) (25 g, 94 mmol) in 1,2-dibromoethane (20 ml) was added dropwise to a solution of **5a** (15 g, 63 mmol) in 1,2-dibromoethane (30 ml) under ice-water cooling. After 4.5 h the reaction mixture was poured into ice-water and extracted with ether. The ethereal layer was washed with water, aq $NaHCO_3$, and finally with brine, and dried ($MgSO_4$). GLPC analysis of the crude product showed mainly three products whose area % were 5, 88, and 6% in the order of the retention time.

The solvent was evaporated and the residue dissolved in DMF (30 ml) was treated with DBU (1.5 g, 10 mmol) under ice-water cooling. After having been stirred for 3.5 h the reaction mixture was poured into ice-cooled dil HCl and extracted with ether. The ethereal layer was worked up as described above. Distillation gave 16 g of ethyl 3-(2,2-dibromoethenyl)-2,2-dimethylcyclopropanecarboxylate (**6a**)[4] (95% purity based on IR, ^1H NMR, GLPC, and GLPC-MS analyses). Bp 104—105 °C/0.28 mmHg (1 mmHg=133.322 Pa). The minor product (6%) with the latest retention time was converted to **6a** by the DBU treatment being attributed to ethyl 2,2-dimethyl-3-(2,2,2-tribromoethyl)cyclopropanecarboxylate (**8a**). Its retention time on GLPC and GLPC-MS data were coincident with those of an authentic sample.[4] Another minor component (5%) with fastest retention time isolated by GLPC separation was assigned to ethyl 3-(2-bromo-2-chloroethenyl)-2,2-dimethylcyclopropanecarboxylate (**7a**). ^1H NMR (CCl_4) δ=6.38 (dd), 5.73 (dd)(total 1H), 4.03 (q, 2H), 2.3—1.5 (m, 2H), 1.4—1.1 (m, 9H). MS *m/z* 281

(M^+), 41 (base). Found: C, 42.43; H, 4.96%. Calcd for $C_{10}H_{14}BrClO_2$: C, 42.66; H, 5.01%.

Halogen Exchange of Ethyl 2,2-Dimethyl-3-(2,2,2-trichloroethyl)cyclopropanecarboxylate (9a).[15] To a solution of **9a** (0.55 g, 2.0 mmol) in dibromomethane (3 ml) was added a solution of $AlBr_3$ (0.53 g, 2.0 mmol) in dibromomethane (1 ml) under ice-water cooling. The composition of the reaction mixture was analysed by GLPC (diasolid ZS) at appropriate time intervals. The products (area %) formed after 45 min were **8a** (62%) and **6a** (29%).

Examination of the Effect of HBr Scavenger. a) Addition of Al Metal: A solution of $AlBr_3$ (0.80 g, 3.0 mmol) in dibromomethane (2 ml) was added to a solution of **9a** (0.55 g, 2 mmol) in dibromomethane under ice-water cooling. Small pieces of Al foil (ca. 50 mg) was added to the reaction mixture. After having been stirred for 7.5 h the reaction mixture was poured into ice-water and extracted with ether. Usual work-up, followed by GLPC (diasolid ZS) assay (octadecane (0.25 g) as an internal standard) gave the results cited in Table 1.

b) Bubbling with Argon Gas at Atmospheric Pressure: After the halogen exchange of **9a** was carried out in a similar manner as described above, argon gas was introduced to the reaction mixture. After 6 h the product yields were determined by GLPC.

c) Bubbling with Argon Gas under Reduced Pressure: The reaction was carried out in a similar manner as described in section b. After argon gas was introduced for 15 min the pressure of the reaction system was gradually reduced to 20 mmHg. The flow of argon gas was controlled so as to maintain moderate bubbling under ice-water cooling. After 3 h the reaction mixture was worked up.

Direct Conversion of Dichloroethenyl Compound 5a to 6a. To a solution of **5a** (0.48 g) in dibromomethane (2 ml) was added dropwise a solution of $AlBr_3$ (0.80 g, 3.0 mmol) in dibromomethane (3 ml) under ice-water cooling. After 1.5 h the pressure of reaction system was reduced to 20 mmHg under moderate argon bubbling for 4 h.

General Procedure for the Reaction of 5a with Various Metal Bromides. A solution of **5a** (0.47 g, 2.0 mmol) in dibromomethane (2 ml) was added dropwise to a mixture of a metal bromide (3.0 mmol) in dibromomethane (3 ml) under ice-water cooling. When no change of the composition of the reaction mixture was observed on GLPC analysis, the reaction temperature was raised to room temperature, 60 °C, and finally to the refluxing temperature. The composition of the mixture was analyzed by GLPC at every temperature.

Halogen Exchange of 5a with Aluminium Compound Other than Commercial $AlBr_3$. a) Al–$BrCH_2CH_2Br$ Method: A small amount of bromine (ca. 40 mg) was added to two pieces (ca. 30 mg) of Al foil (Showa Aluminium Co., cut into small pieces) in 1,2-dibromoethane (5 ml) and the mixture was heated by open flame until an exothermic reaction started. After the reaction had started, remaining Al foil (total 0.41 g, 15 mmol) was added one by one. After all Al foil had been dissolved, the resulting black mixture was transferred into a dropping funnel which was attached to a second flask in which a solution of **5a** (2.4 g, 10 mmol) in 1,2-dibromoethane (10 ml) was placed. After the addition of the complex prepared above under ice-water cooling, the reaction mixture was allowed to warm to 20 °C. The reaction mixture was stirred for 9.5 h and then poured into ice-water and worked up as usual. Distillation of the crude product gave 2.7 g of a pale yellow oil which was composed of **6a** (89%), **7a** (3%), and **8a** (5%), bp 101—106.5 °C/0.27 mmHg.

b) Al–Br_2 Method: Bromine (2.6 g, 16 mmol) was added to one piece of Al foil suspended in dibromomethane (8 ml) and the mixture was heated by open flame until an exothermic reaction started. Then, remaining Al foil (total 0.43 g, 16 mmol) was added one by one. After all Al foil had been dissolved, the resulting black solution was transferred into a syringe and was added dropwise to a solution of **5a** (2.4 g, 10 mmol) in dibromomethane under ice-water cooling. After the addition was completed, the reaction mixture was allowed to warm to 10 °C. Then, the reaction mixture was stirred overnight at room temperature. GLPC analysis showed that the reaction mixture was composed of **6a** (47%) and **8a** (35%) along with a small amount of **7a**.

c) Al–HBr Method: To a mixture of Al metal [Al ribbon (Merck, GR) was cut into small pieces] (0.40 g, 15 mmol) in dibromomethane (10 ml) was introduced HBr gas through gas inlet tube at 30 °C (water bath). After 5 min an exothermic reaction started and brown solids formed gradually. After all Al metal had disappeared, the resulting brown suspension was heated until the reaction mixture became a brown clear solution. Then, the mixture was cooled with ice-water and a solution of **5a** (2.4 g, 10 mmol) in dibromomethane (10 ml) was added dropwise to the cooled mixture. The introduction of HBr was continued until the color of the reaction mixture changed to reddish black (ca. 10 min after the addition of the substrate). After the completion of the reaction was confirmed by GLPC (2 h after the addition of the substrate), the pressure of the reaction system was reduced to 20 mmHg, argon gas being gently introduced. After 2.5 h (GLPC check) the reaction mixture was worked up. Distillation afforded 2.8 g (86%) of **6a**, bp 108—110 °C/0.3 mmHg (purity 96%).

d) $AlCl_3$–HBr Method: To a suspension of $AlCl_3$ (Kishida Kagaku, GR) (0.99 g, 7.5 mmol) in dibromomethane (6 ml) was introduced HBr gas at 30 °C. After 30 min a solution of **5a** (1.2 g, 5.1 mmol) in dibromomethane (4 ml) was added dropwise to the resulting suspension under ice-water cooling. The introduction of HBr was continued until the color of the reaction mixture changed to reddish black (ca. 1.5 h after the addition of the substrate). After the completion of the reaction was confirmed by GLPC (4 h after the addition of the substrate), the pressure of the reaction system was reduced to 20 mmHg under argon bubbling. After 3.5 h, the reaction mixture was worked up. Distillation afforded 1.5 g (90%) of **6a**, bp 105—109 °C/0.25 mmHg (purity 95%).

Methyl 3-(2,2-Dibromoethenyl)-2,2-dimethylcyclopropanecarboxylate (6b). This reaction was carried out as described above (Al–HBr method), starting from methyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate (**5b**) (2.2 g, 10 mmol) and Al metal (0.40 g, 15 mmol). Distillation of crude product afforded 2.8 g (90%) of **6b**, bp 101—103 °C/0.26 mmHg (purity 96%). The structure was confirmed by the comparison with an authentic sample.[15]

3-(2,2-Dibromoethenyl)-2,2-dimethylcyclopropanecarboxylic Acid (6c). a) $AlBr_3$ Method: A solution of 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylic acid (**5c**) (trans 100%)[15] (4.2 g, 20 mmol) in dibromomethane (20 ml) was added dropwise to a solution of $AlBr_3$ (8.0 g, 30 mmol) in dibromomethane (20 ml) over a period of 15 min under ice-water cooling. After the addition was completed, argon gas was introduced to the reaction mixture through syringe needle for 15 min. The pressure of the reaction system was then gradually reduced to 20 mmHg under argon bubbling.

After 2.5 h the reaction mixture was poured into ice-water. Then, dil HCl was added and the resulting mixture was extracted with ether-AcOEt (ca. 4:1). The organic layer was washed with dil HCl and brine, and then dried ($MgSO_4$). After removal of the solvents, the crude product was extracted with hot hexane and insoluble parts were filtered off. Removal of the solvent afforded 5.5 g (93%) of yellow solids assigned to **6c** by the comparison of the spectral data with those of authentic sample.[5a,15] Purity was 96%, and isomeric purity was 100% trans based on GLPC analysis after esterification with CH_2N_2. Mp 118—120 °C (hexane). lit,[5a] 117—118 °C (ethanol-water). Similarly, 5.6 g (94%) of *cis*-**6c** (purity 96%, 100% cis) was obtained starting from 4.2 g of 100% *cis*-**5c**. The isomeric purity was also checked by GLPC analysis. Mp 108—111 °C (hexane). lit,[15] 112—114 °C (hexane). Halogen exchange of (−)-*trans*-**5c** was similarly carried out, starting from 2.0 g (9.5 mmol) of (−)-*trans*-**5c** ($[\alpha]_D=-36.3°$ ($CHCl_3$), lit,[17] $[\alpha]_D=-36.6°$ ($CHCl_3$)) by means of $AlBr_3$ (3.8 g, 14 mmol). After extraction with hot hexane, removal of the solvent afforded 2.6 g (93%) of yellow solids. GLPC analysis of the product after esterification by CH_2N_2 showed that the product obtained was composed of 96% of **6c** (trans 100%). $[\alpha]_D=-37.5°$ ($CHCl_3$). lit,[5b] $[\alpha]_D=-40.5°$ ($CHCl_3$).

b) Al–HBr Method: An aliquot of Al ribbon cut into small pieces (5.1 g in total, 0.19 mmol) in dibromomethane (125 ml) was warmed to 30 °C and HBr gas was introduced. When an exothermic reaction started, the rest of Al metal was added portionwise to maintain the reaction temperature between 60—65 °C. After all Al metal had dissolved (ca. 1.5 h), the gas inlet tube was replaced by a dropping funnel through which a solution of *cis*-**5c** (26 g, 0.13 mol) in dibromomethane (100 ml) was added dropwise at 5—7 °C. When the completion of the halogen exchange was confirmed by GLPC (ca. 2 h from the start of the addition), the pressure in the reaction flask was reduced to 20 mmHg under usual argon bubbling (ice-water bath). After 4.5 h (GLPC check) the reaction mixture was worked up. Removal of the solvent afforded 33 g (89%) of *cis*-**6c** as brown solids, whose purity was 93% on GLPC, mp 105—108 °C (hexane).

3-(1-Bromo-1-methylethyl)-5,5-dichloro-4-pentenoic Acid (12). A solution of BBr_3 (0.6 ml) in dibromomethane (4 ml) was added dropwise to a solution of **5a** (0.95 g, 4.0 mmol) in dibromomethane under ice-water cooling. After the addition was completed, the reaction mixture was allowed to warm to room temperature and stirred overnight. The mixture was poured into cold dil HCl and extracted with ether-AcOEt (4:1). The organic layer was washed with water (twice) and brine, and dried ($MgSO_4$). Recrystallization (hexane) gave 0.75 g (65%) of **12** as slightly brown crystals, (needles), mp 81—82 °C. IR (KBr disk): 3200—2600, 1700, 1620, 1310, 875 cm^{-1}. ^1H NMR (CCl_4) $\delta=5.94$ (d, 1H), 3.25—2.8 (m, 2H), 2.48 (dd, 1H), 1.84 (s, 3H), 1.77 (s, 3H). MS *m/z* 288 (M^+), 122 (base). Found: C, 33.32; H, 3.79%. Calcd for $C_8H_{11}BrCl_2O_2$: C, 33.14; H, 3.82%.

3-(2,2-Dichloroethenyl)-4-methyl-4-pentanolide (13). The reaction of **5a** (4.7 g, 20 mmol) with BBr_3 (3.0 ml) in dibromomethane was carried out as described above. The reaction mixture after having been stirred overnight was poured into ice-water and extracted with ether. The ethereal layer was washed with brine and aq $NaHCO_3$ (three times). The aqueous layer was extracted with ether and the combined ethereal layer was washed with brine (twice) and dried ($MgSO_4$). Recrystallization (hexane : AcOEt=5:1) afforded 2.6 g (63%) of **13**, mp 118—119 °C (lit,[14] 115—117 °C). IR (neat): 1770, 1625, 1280, 1260, 1100, 890 cm^{-1}. ^1H NMR (CCl_4) $\delta=5.89$ (d, 1H), 3.36 (m, 1H), 2.95—2.3 (m, 2H), 1.52 (s, 3H), 1.35 (s, 3H). MS *m/z* 208 (M^+), 122 (base).

Ethyl 3-(1-Bromo-1-methylethyl)-5,5-dichloro-4-pentenoate (14). After the overnight reaction of **5a** (2.4 g, 10 mmol) with BBr_3 (1.5 ml) the reaction mixture was concentrated in vacuo. The residue was dissolved in 3 ml of dry ethanol. After 30 min the resulting mixture was diluted with ether, washed with water (twice) and brine, and dried ($MgSO_4$). Distillation of the crude product afforded 2.8 g (88%) of **14**, bp 93—94 °C/0.17 mmHg. IR (neat): 1740, 1620, 1255, 1175, 1115, 880 cm^{-1}. ^1H NMR (CCl_4) $\delta=5.89$ (d, 1H), 4.12 (q, 2H), 3.15—2.65 (m, 2H), 2.35 (dd, 1H), 1.82 (s, 3H), 1.77 (s, 3H), 1.26 (t, 3H). MS *m/z* 317 (M^+), 237 (base). Found: C, 37.89; H, 4.66%. Calcd for $C_{10}H_{15}BrCl_2O_2$: C, 37.77; H, 4.75%.

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13) The addition of hydrogen bromide to dichloroethenyl compound **5a** did not occur in the absence of the aluminium ion. Thus, coordination of alminium trihalide most probably to carbonyl oxygen first occurred and then assisted the addition of HBr. The coordinated aluminium trihalide would be inactive for halogen exchange.

14) Exact optical purity was not determined. However, purified product (purity 99% on GLPC) by repeated

recrystallization had specific rotation of −40.3° which was almost equal to the one of pure (−)-*trans*-**6c**.

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