oxygenated toluene and 5 mg of hydroquinone. The reaction mixture was heated to reflux under an argon atmosphere and maintained at reflux for 18 h. Analysis of the mixture by capillary gas chromatography at 120 °C revealed the presence of two products with t_R 3.10 (78%) and 3.41 min (22%). The solution was concentrated to a volume of 5 mL, and 40 mg of maleic anhydride (0.40 mmol) was added with stirring. The mixture was allowed to react for 2 h at ambient temperature at which time the product with t_R 3.41 min was absent. The reaction mixture was concentrated in vacuo, and isolation of the product was achieved by flash chromatography. Elution on silica gel with petroleum ether/ether (40:1) produced 116 mg (53%) of **40** with R_f 0.18 as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$), assignments as in Figure 5, δ 6.04 (dd, J = 2.9, 5.6 Hz, 1 H, H_1), 5.86 (dd, J = 2.7, 5.6 Hz, 1 H, H_2), 2.83–2.88 (m, 1 H, H_3), 2.57 (br s, 1 H, H_4), 2.37(d, J = 4.9 Hz, H_5), 2.18–2.26 (m, 2 H, H_6, H_7), 1.65–1.80 (m, 2 H, H_8, H_9), 1.33–1.48 (m, 1 H, H_{10}), 1.37 (s, 9 H, H_{11}), 1.13–1.23 (m, 1 H, H_{12}); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ 172.6, 133.7, 132.9, 79.6, 63.1, 53.1, 50.8, 50.2, 38.9, 34.4, 28.4, 22.1; IR (neat) 3060, 2975, 2870, 1733, 1370, 1240, 1160, 1120 cm^{-1}. Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15. Found: C, 76.12; H, 9.16.

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Registry No. **1c**, 117471-71-3; **2**, 117471-72-4; **9**, 3709-08-8; **10**, 102536-89-0; **11**, 117471-73-5; **12**, 117557-95-6; **13**, 117471-74-6; **14a**, 54911-85-2; **14c**, 14194-86-6; **14d**, 62592-78-3; **15a**, 96251-91-1; **15c**, 117471-84-8; **15d**, 117471-86-0; **16a**, 117471-75-7; **16b**, 117471-82-6; **16c**, 117471-83-7; **16d**, 117471-85-9; **17a**, 64277-92-5; **17b**, 117471-87-1; **17c**, 117471-88-2; **17d**, 117471-89-3; **20**, 117471-76-8; **21**, 117471-77-9; **23**, 117471-92-8; **26**, 117471-78-0; **27**, 117471-79-1; **31**, 117471-91-7; **34**, 117471-80-4; **35**, 117557-96-7; **37**, 117471-90-6; **40**, 117471-81-5; CpMgBr, 34766-86-4; CpMgCl, 34766-85-3; $(EtO)_2POCH_2CO_2C(CH_3)_3$, 27784-76-5; γ-butyrolactone, 96-48-0; cyclopentadiene, 542-92-7; triethyl phosphonoacetate, 867-13-0.

Reductive Addition of Polyhalomethanes and Their Related Compounds to Aldehydes and 1,2-Elimination of the Coupling Products in a Pb/Al Bimetal Redox System

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A Pb/Al bimetal system was used to carry out reductive addition of tetrachloromethane, tetrabromomethane, bromotrichloromethane, trichloroacetamide, and trichloroacetonitrile to aldehydes. Subsequent 1,2-elimination of the halogen atom and hydroxyl group from the coupling products was also performed with the Pb/Al bimetal system. The technology was successfully applied to stereocontrolled syntheses of ethyl *trans*- and *cis*-3-(2,2-dihaloethenyl)-2,2-dimethylcyclopropanecarboxylates.

Reductive addition of polyhaloalkanes to carbonyl compounds is important for making carbon–carbon bonds in organic synthesis, and various kinds of low-valent metals have been employed for this purpose.[1] Although the reductive addition of tetrahalomethanes to aldehydes provides direct access to trihalomethyl carbinols, very few metals are known to be effective in such reactions, presumably due to the instability of intermediary metal carbenoids.[2] To our knowledge, the reductive addition of tetrabromomethane to aldehydes with SnF_2[3] is the only example hitherto disclosed.

Base-induced addition of chloroform to aldehydes has been studied as a route to trichloromethyl carbinols,[4,5] but the yields of the trichloromethyl carbinols often suffer due to undesirable side reactions. The reaction of aromatic

Scheme I

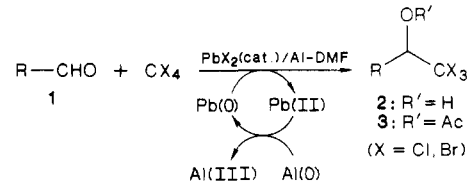


Table I. Effect of Metal Salts in the Reductive Addition of CCl_4 to Aldehyde 1a[a]

entry	metal salt, mmol	time, h	yield,[b] %
1	$PbBr_2$ (0.1)	3	94
2	$PbCl_2$ (0.1)	3.5	97
3	Pb (0.1)	5	95
4	none	10	– (93[c])
5	$SnCl_2$ (0.1)	12	– (98[c])
6	$SnCl_2$ (0.5)	5	92
7	$BiCl_3$ (0.1)	10	– (98[c])
8	$GeCl_4$ (0.1)	10	– (91[c])
9	$ZnCl_2$ (0.1)	10	– (88[c])

[a] Carried out with **1a** (1 mmol), CCl_4 (2 mmol), and Al (1.2 mmol) in DMF (5 mL) at room temperature. [b] Isolated yields based on aldehyde **1a**. [c] Recovered **1a**.

(1) (a) Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* **1972**, 3769. (b) Villieras, J.; Bacquet, C.; Normant, J. F. *J. Organomet. Chem.* **1975**, *97*, 325. (c) Santini, G.; Le Blanc, M.; Riess, J. G. *J. Chem. Soc., Chem. Commun.* **1975**, 678. (d) Furet, C.; Servens, C.; Pereyre, M. *J. Organomet. Chem.* **1975**, *102*, 423. (e) Fujita, M.; Morita, T.; Hiyama, T. *Tetrahedron Lett.* **1986**, *27*, 2135 and references cited therein.

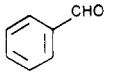
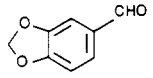
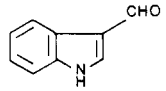
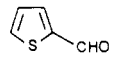
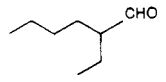
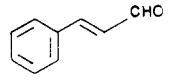
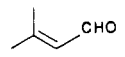
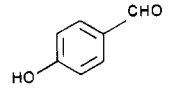
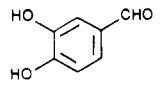
(2) (a) Haszeldine, R. N. *J. Chem. Soc.* **1954**, 1273. (b) Kirmse, W. *Carbene Chemistry*, 2nd ed.; Academic Press: New York, 1971. (c) Taguchi, H.; Yamamoto, H.; Nozaki, H. *J. Am. Chem. Soc.* **1974**, *96*, 3010.

(3) Mukaiyama, T.; Yamaguchi, M.; Kato, *J. Chem. Lett.* **1981**, 1505.

(4) Addition by use of chemical bases: (a) Weizmann, Ch.; Bergmann, E.; Sulzbacher, M. *J. Am. Chem. Soc.* **1948**, *70*, 1189. (b) Bergmann, E. D.; Ginsburg, D.; Lavie, D. *Ibid.* **1950**, *72*, 5012. (c) Kaspar, E.; Wiechert, R. *Chem. Ber.* **1958**, *91*, 2664. (d) Merz, A.; Tomahogh, R. *Ibid.* **1977**, *110*, 96 and references cited therein.

0022-3263/89/1954-0444$01.50/0

Table II. Reductive Addition of CCl_4 to Aldehydes in a Pb/Al Bimetal System[a]

entry	1	CCl_4, mmol	Al, mmol	time, h	product 2 yield,[b] %
1	 1b	2.0	1.2	3.5	95
2	 1c	2.0	1.2	3.5	97
3	 1d	3.0	2.0	3	90
4	 1e	2.0	1.2	2	98
5	 1f	2.0	1.2	5	88
6	 1g	2.0	1.2	3.5	88
7	 1h	2.0	1.2	3	80
8	 1i	4.0	3.0	6	93
9	 1j	4.0	4.0	5	75

[a] Carried out with aldehydes 1 (1 mmol) and $PbBr_2$ (0.1 mmol) in DMF (5 mL) at room temperature. [b] Isolated yields based on aldehydes 1.

compounds with chloral in the presence of Lewis acids or bases can provide 1-aryl-2,2,2-trichloroethanols[6] but is limited in scope because of mixtures of regioisomers.

In previous papers we disclosed a novel Pb/Al bimetal system that reductively couples allyl halides to various electrophiles including aldehydes, ketones, acetals, and imines.[7] In addition, we found that the Pb/Al bimetal system can effect 1,2-elimination of a halogen atom and a hydroxyl group from the trihalomethyl carbinols **2**, leading to 1,1-dihaloethene derivatives **4**.[8] The products **2** can be transformed to α-methoxy or α-hydroxy carboxylic acids,[9] α-amino acids,[10] and α-chloroacetic acids,[11] while the 2-phenyl-1,1-dihaloethenes **4** (R = aryl) are key precursors in the phenylacetic acid synthesis.[12]

In this paper, we describe a straightforward access to trihalomethyl carbinols **2** and 1,1-dihaloethenes **4** as well as stereocontrolled syntheses of ethyl *trans*- and *cis*-3-(2,2-dihaloethenyl)-2,2-dimethylcyclopropanecarboxylates.

Results and Discussion

Reductive Addition of Polyhalomethanes and Their Related Compounds to Aldehydes in a $PbBr_2$(cat.)/Al–DMF System. The reductive addition of tetrachloromethane to aldehyde **1a** (R = 4-ClC_6H_4) was performed as follows (Scheme I): A mixture of **1a** and tetrachloromethane (1:2) in *N*,*N*-dimethylformamide (DMF) was treated with a catalytic amount of lead(II) bromide

(5) Addition by use of electrogenerated bases: (a) Karrenbrock, F.; Schäfer, H. J. *Tetrahedron Lett.* **1978**, 1521. (b) Shono, T.; Kashimura, S.; Ishizaki, K.; Ishige, O. *Chem. Lett.* **1983**, 1311. (c) Shono, T.; Kise, N.; Masuda, M.; Suzumoto, T. *J. Org. Chem.* **1985**, *50*, 2527. (d) Sibille, S.; d'Incan, E.; Leport, L.; Perichon, J. *Tetrahedron Lett.* **1986**, *27*, 3129 and references cited therein.

(6) (a) Reeve, W.; Mutchler, J. P.; Liotta, C. L. *Can. J. Chem.* **1966**, *44*, 575. (b) Casiraghi, G.; Casnati, G.; Sartori, G.; Catellani, M. *Synthesis* **1979**, 824. (c) Grochowski, E.; Rostafinska, B.; Szelejewski, W. *Przem. Chem.* **1985**, *64*, 476; *Chem. Abstr.* **1986**, *104*, 224641p.

(7) (a) Tanaka, H.; Yamashita, S.; Hamatani, T.; Ikemoto, Y.; Torii, S. *Synth. Commun.* **1987**, *17*, 789. (b) Tanaka, H.; Yamashita, S.; Ikemoto, Y.; Torii, S. *Chem. Lett.* **1987**, 673. (c) Tanaka, H.; Yamashita, S.; Ikemoto, Y.; Torii, S. *Tetrahedron Lett.* **1988**, *29*, 1721.

(8) (a) Merz, A. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 57. (b) Wolf, R.; Steckhan, E. *J. Chem. Soc., Perkin Trans. 1* **1986**, 733.

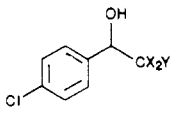
(9) (a) Reeve, W.; Woods, C. W. *J. Am. Chem. Soc.* **1960**, *82*, 4062. (b) Compere, E. L., Jr. *J. Org. Chem.* **1968**, *33*, 2565. (c) Compere, E. L., Jr.; Shockravi, A. *Ibid.* **1978**, *43*, 2702.

(10) Reeve, W.; Fine, L. W. *J. Org. Chem.* **1964**, *29*, 1148.

(11) Reeve, W.; Mckee, J. R.; Brown, R.; Lakshmanan, S.; Mckee, G. A. *Can. J. Chem.* **1980**, *58*, 485.

(12) Torii, S.; Tanaka, H.; Yamashita, S.; Yamanoue, M.; Taniguchi, M.; Sasaoka, M. *Chem. Express* **1987**, *2*, 615.

Table III. Reductive Addition of Polyhaloalkanes to 4-Chlorobenzaldehyde[a]

entry	haloalkane, mmol	Al, mmol	time, h	product	yield,[b] %
1	CBr_4 (3.4)	3.0	9	 **2k** (X = Y = Br)	76
2	$CBrCl_3$ (4.0)	3.0	5	**2a** (X = Y = Cl)	86
3	CCl_3CONH_2 (2.0)	1.3	6[c]	**2m** (X = Cl, Y = $CONH_2$)	63 (10[d])
4	CCl_3CN (2.0)	1.3	3.5[e]	**2n** (X = Cl, Y = CN)	62 (23[d])
5	CCl_3COOEt (2.0)	1.5	2	**2o** (X = Cl, Y = COOEt)	27 (27[f])

[a] Carried out with 4-chlorobenzaldehyde (**1a**; 1 mmol) and $PbBr_2$ (0.1 mmol) in DMF (5 mL) at room temperature. [b] Isolated yields based on aldehyde **1a**. [c] Ca. 60 °C. [d] Recovered **1a**. [e] 10–15 °C. [f] Ethyl 2-chloro-3-(4-chlorophenyl)-3-hydroxypropionate (**5o**).

and aluminum in slight excess (1.2 equiv) at ambient temperature, affording the coupling product **2a** (R = 4-ClC_6H_4; X = Cl) in 94% yield.

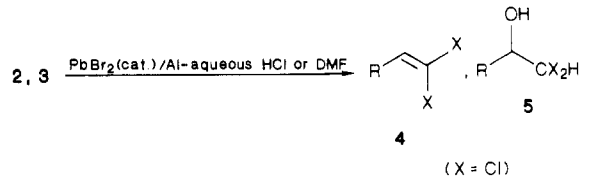
As shown in Table I, satisfactory results were also obtained by use of a combination of lead(II) chloride or lead powder with aluminum (entries 2 and 3). The lead is indispensable for this reaction, since the reaction in its absence did not give any amount of **2a** (entry 4). In place of lead(II) salts, tin(II) chloride is also usable but less reactive than lead(II) salts; actually, more than 5-fold amounts of tin(II) chloride were necessary to complete the reaction (entries 5 and 6). When either bismuth(III) chloride, germanium(IV) chloride, or zinc(II) chloride was used in place of lead(II) salts, the reductive addition of tetrachloromethane to aldehyde **1a** failed, giving the recovered **1a** (entries 7–9). The effect of solvent is also remarkable; other protic or aprotic solvents so far investigated (MeOH, MeOH–H_2O (1:1), MeCN, THF, or THF–DMF (25:1)) failed to provide **2a**.

Next, we applied the Pb/Al bimetal system to the addition of tetrachloromethane to a variety of aldehydes **1** (Table II). The reaction of tetrachloromethane with aldehydes **1b–f** proceeded efficiently (entries 1–5), and 1,2-addition took place with α,β-unsaturated aldehydes **1g,h** (entries 6 and 7). Notably, addition to aldehydes **1i,j** can be carried out without protection of hydroxyl group by employing excess tetrachloromethane and aluminum (entries 8 and 9). On the other hand, ketones are less reactive; for example, acetophenone afforded only 18% yield of the coupling product together with unreacted acetophenone (69%) even after the reaction with excess tetrachloromethane (5 equiv) for 10 h.

The reductive addition of polyhalomethanes and their derivatives to aldehyde **1a** (R = 4-ClC_6H_4) in the Pb/Al bimetal system was also examined (Table III). Tetrabromomethane reacted with **1a** under similar conditions to afford the coupling product **2k** (X = Y = Br) in 76% yield (entry 1). Bromotrichloromethane underwent exclusive C–Br bond fission, yielding the corresponding trichloromethyl carbinol **2a** (entry 2). Trichloroacetamide is less reactive than tetrahalomethanes, requiring heating at 60 °C (entry 3) to obtain the coupling product **2m** (63%). In contrast, the reaction of **1a** with trichloroacetonitrile proceeds exothermically at 10–15 °C (entry 4). In the reaction of **1a** with ethyl trichloroacetate, the aldehyde addition and further reduction of the dichloromethylene group of the coupling product **2o** took place competitively, affording the desired product **2o** (27%) together with ethyl 2-chloro-3-(4-chlorophenyl)-3-hydroxypropionate (**5o**) (27%).

Although the reaction mechanism of the Pb/Al bimetal redox system has not yet been clarified, it presumably involves lead(0) reduction of polyhalomethanes to provide an organolead complex (e.g. CX_3PbX),[13] which would, in turn, react with aldehydes **1** to give the coupling products **2**. Regeneration of lead(0) by reduction of lead(II) with aluminum metal would complete the catalytic cycle (Scheme I). It is noteworthy, however, that commercially available lead powder (>99.9% pure) alone was not effective for this reductive addition at all. This fact suggests that lead(0) freshly generated on the aluminum surface is important for the coupling reaction.[14]

Scheme II



1,2-Elimination of the Coupling Products and Related Compounds in a $PbBr_2$(cat.)/Al System. Reductive 1,2-elimination of trichloromethyl carbinols **2** in the Pb/Al bimetal system can be readily achieved by change of the reaction medium (Scheme II).

The treatment of trichloromethyl carbinol **2a** with lead(II) bromide (0.05 equiv) and aluminum (1.5 equiv) in methanol containing aqueous 35% hydrochloric acid (2 equiv) at 50–60 °C afforded the corresponding 1,1-dichloroethene **4a** in 83% yield (entry 1 in Table IV). Aryl- or vinyl-substituted 1,1-dichloroethenes **4b,c,g,i** were also prepared in good yields (entries 4, 7, 13, and 16). In contrast, the alkyl-substituted homologue **2f** was reductively dechlorinated to afford the dichloromethyl carbinol **5f** (50%), indicating that the hydroxyl group of **2f** is not as labile as in the benzylic or allylic alcohols of **2a–c,g,i**.

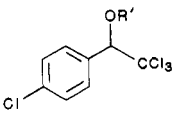
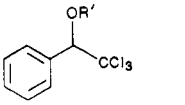
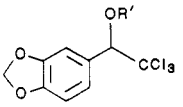
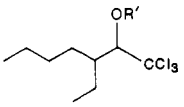
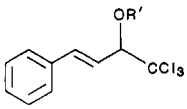
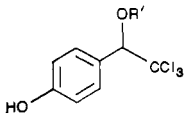
1,2-Elimination of the trichloromethyl carbinols **2** was performed more efficiently by acetylation of the hydroxyl groups prior to the reduction in the Pb/Al bimetal system. Thus, 1,2-elimination of the acetates **3a–c,g** as well as alkyl-substituted acetate **3f** in a $PbBr_2$(cat.)/Al–DMF system took place smoothly at room temperature to afford the corresponding 1,1-dichloroethenes **4a–c,f,g** in 64–84% yields (entries 2, 5, 8, 11, and 14), whereas trichloromethyl carbinols **2** afforded only the hydrogenation products **5** in 11–64% yields (entries 3, 6, 9, 12, and 15).

In all of the entries described above, the absence of catalytic lead(II) bromide resulted in total recovery of

(13) Analogous lead(II) complexes, e.g., CH_2=$CHCH_2PbBr$ and CF_3CCl_2PbCl, have been postulated as potential intermediates in the reductive coupling of halides with various electrophiles: ref 7 and Tanaka, H.; Yamashita, S.; Katayama, Y.; Torii, S. *Chem. Lett.* **1986**, 2043.

(14) Low valent metals generated in metal salt/metal combinations, e.g., NiX_2/Li,[a] $SnCl_2$/Al,[b] $TiCl_4$/Mg,[c] etc., have been found to be highly reactive and useful reducing agents for various synthetic purposes: (a) Inaba, S.; Matsumoto, H.; Rieke, R. D. *J. Org. Chem.* **1984**, *49*, 2093. (b) Uneyama, K.; Kamaki, N.; Moriya, A.; Torii, S. *J. Org. Chem.* **1985**, *50*, 5396. (c) Betschart, C.; Seebach, D. *Helv. Chim. Acta* **1987**, *70*, 2215 and references cited therein.

Table IV. 1,2-Elimination of 2 or 3 in a Pb/Al Bimetal System

entry	2 or 3		conditions[a]	time, h	product (yield,[b] %) 4	5
1		**2a** (R′ = H)	A	7	83	9
2		**3a** (R′ = Ac)	B	3.5	84	
3		**2a** (R′ = H)	B	4.5		64
4		**2b** (R′ = H)	A	14	85	
5		**3b** (R′ = Ac)	B	8	75	
6		**2b** (R′ = H)	B	3		45
7		**2c** (R′ = H)	A	8	70	26
8		**3c** (R′ = Ac)	B	6	84	
9		**2c** (R′ = H)	B	4		11
10		**2f** (R′ = H)	A	10		50
11		**3f** (R′ = Ac)	B	6	64	
12		**2f** (R′ = H)	B	8		14
13		**2g** (R′ = H)	A	6	89	
14		**3g** (R′ = Ac)	B	3.5	84	
15		**2g** (R′ = H)	B	1		39
16		**2i** (R′ = H)	A	9	87	

[a] A: Carried out with **2** (1 mmol), $PbBr_2$ (0.05–0.1 mmol), Al (1.5 mmol), and aqueous 35% HCl (2 mmol) in MeOH (2 mL) at 50–60 °C. B: Carried out with **2** or **3** (1 mmol), $PbBr_2$ (0.1 mmol), and Al (1.2 mmol) in DMF (5 mL) at room temperature. [b] Isolated yields based on **2** or **3**.

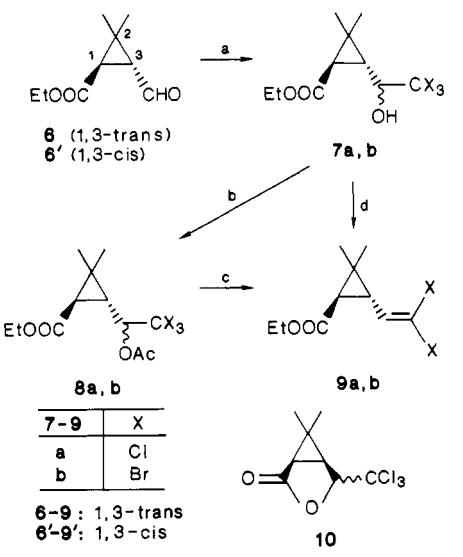
starting materials **2**. It is likely that low-valent lead generated in the Pb/Al bimetal system induces the 1,2-elimination in the analogous fashion as described for the reductive addition of polyhalomethanes to aldehydes **1** (Scheme I).

Synthesis of Ethyl *trans*- and *cis*-3-(2,2-Dihaloethenyl)-2,2-dimethylcyclopropanecarboxylates. The synthetic pyrethroid insecticides bearing (2,2-dichloroethenyl)- and (2,2-dibromoethenyl)cyclopropanecarboxylates (**9** and **9′**) as the acid components play important roles as pesticides in agriculture.[15] The stereochemistry about the cyclopropane ring influences both the spectrum and level of insecticidal activities. Although many stereocontrolled syntheses have appeared in the literatures,[16] it is still difficult to attain the high stereoselectivities under simple operations.

The one-carbon homologation of aldehydes with polyhalomethanes using the Pb/Al bimetal system enabled us to complete a stereospecific synthesis of ethyl *trans*- or *cis*-3-(2,2-dihaloethenyl)-2,2-dimethylcyclopropanecarboxylate (**9** or **9′**) with ethyl *trans*- and *cis*-3-formyl-2,2-dimethylcyclopropanecarboxylates (**6** and **6′**)[17] as starting materials as outlined in Scheme III.

Synthesis of ethyl *trans*-3-(2,2-dihaloethenyl)-2,2-dimethylcyclopropanecarboxylates (**9**) was performed by the following two- or three-step operations; the reaction of a mixture of tetrachloromethane and ethyl *trans*-3-formyl-2,2-dimethylcyclopropanecarboxylate (**6**) with a catalytic amount of lead(II) bromide (0.1 equiv) and aluminum (1.5 equiv) in DMF afforded the corresponding coupling product **7a** (87%), and subsequent reduction with the same $PbBr_2$(cat.)/Al system in ethanol containing sulfuric acid at 50–60 °C afforded ethyl *trans*-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate (**9a**) in 78% yield. Alternatively, after acetylation of the hydroxyl group

Scheme III[a]



[a] (a) $CX_4/PbBr_2$(cat.)/Al–DMF; (b) Ac_2O/pyridine; (c) $PbBr_2$(cat.)/Al–DMF; (d) $PbBr_2$(cat.)/Al–concentrated H_2SO_4–EtOH.

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of **7a** (92%), the acetate **8a** was treated with the $PbBr_2$-(cat.)/Al reagent in DMF to afford **9a** in 82% yield. Similarly, the syntheses of 2,2-dibromoethenyl analogue **9b** and ethyl *cis*-3-(2,2-dihaloethenyl)-2,2-dimethylcyclopropanecarboxylates (**9'**) were accomplished in the indicated yields and conditions.

Throughout above reaction sequence, any detectable amount of epimerization was not observed. Further applications of the Pb/Al bimetal system are now in progress.

Experimental Section

Melting points were determined in open capillaries and are uncorrected. IR spectra were taken on a JASCO IRA-1 grating spectrometer. ^1H NMR spectra were obtained on Hitachi R-24 (60 MHz) and/or Varian VXR-500 (500 MHz) spectrometers. ^{13}C NMR spectra were obtained on JEOL FX-100 (25.05 MHz) and/or Varian VXR-500 (126 MHz) spectrometers. Chemical shifts are expressed in parts per million downfield from Me_4Si used as an internal standard. High-resolution mass spectra (HRMS) were obtained on a JMX-DX-303 HF spectrometer. Elemental analyses were performed with a YANACO CHN CORDER MT-3 instrument. Thin-layer chromatography was performed on Merck Kieselgel $60F_{254}$ precoated silica gel plates. Column chromatography was carried out with Merck Kieselgel 60 (silica gel) with hexane–EtOAc as an eluent.

Materials. Tetrachloromethane was obtained by distillation from P_2O_5 and stored over 4-Å molecular sieves. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. Reagent grade $PbBr_2$, $PbCl_2$, Pb, $SnCl_2$, $BiCl_3$, $GeCl_4$, $ZnCl_2$, and Al foil were used. Anhydrous *N,N*-dimethylformamide (DMF) was obtained by distillation from calcium hydride and stored over 4-Å molecular sieves.

General Procedure. Reductive Addition of Polyhalomethanes and Their Related Compounds to Aldehydes. A representative reaction procedure is as follows. Into a mixture of $PbBr_2$ (37 mg, 0.1 mmol) and finely cut Al foil (32 mg, 1.2 mmol) in DMF (5 mL) were added 4-chlorobenzaldehyde (**1a**) (141 mg, 1.0 mmol) and tetrachloromethane (0.20 mL, 2.0 mmol), and the mixture was stirred at ambient temperature until most of **1a** was consumed (3 h). The reaction was quenched with aqueous 5% hydrochloric acid, and the mixture was extracted with EtOAc (6 mL × 5). The combined extracts were washed with aqueous $NaHCO_3$ (6 mL) and brine (6 mL × 4), dried over Na_2SO_4, and concentrated. The residue was chromatographed on a silica gel column (hexane/EtOAc, 5/1) to give 2,2,2-trichloro-1-(4-chlorophenyl)ethanol (**2a**) (244 mg, 94%) as a colorless liquid.

The reaction of tetrachloromethane with aldehyde **1a** using a combination of $PbCl_2$, Pb powder, $SnCl_2$, $BiCl_3$, $GeCl_4$, or $ZnCl_2$ with Al foil was carried out under the conditions shown in Table I. In a similar manner, reductive addition of tetrachloromethane to a variety of aldehydes **1** in the Pb/Al bimetal system was carried out (Table II). The reaction of 4-chlorobenzaldehyde (**1a**) with polyhalomethane derivatives was carried out under the conditions shown in Table III.

Acetylation of the Coupling Products 2. Acetylation of **2** was carried out with pyridine/Ac_2O at ambient temperature. Usual workup of the reaction mixtures afforded the corresponding acetates **3** in 90–97% yields.

1,2-Elimination of the Coupling Products 2 and Related Compounds 3. Method A. A typical reaction procedure is as follows. Into a mixture of $PbBr_2$ (19 mg, 0.05 mmol), finely cut Al foil (41 mg, 1.5 mmol), and aqueous 36% hydrochloric acid (0.17 mL, 2 mmol) in methanol (2 mL) was added 2,2,2-trichloro-1-(4-chlorophenyl)ethanol (**2a**) (260 mg, 1.0 mmol), and the mixture was stirred at 50–60 °C until most of **2a** was consumed (7 h). The reaction mixture was freed of most of methanol under reduced pressure, poured into ice-cold water (ca. 10 mL), and extracted with hexane–ether (1:1) (6 mL × 4). The combined extracts were washed with aqueous $NaHCO_3$ (6 mL × 2) and brine (6 mL × 2), dried over Na_2SO_4, and concentrated. The residue was chromatographed on a silica gel column (hexane/EtOAc, 20/1) to give 4-chloro-1-(2,2-dichloroethenyl)benzene (**4a**) (172 mg, 83%) together with 1-(4-chlorophenyl)-2,2-dichloroethanol (**5a**) (20 mg, 9%). The reaction conditions and results are summarized in Table IV (entries 1, 4, 7, 10, 13, and 16).

Method B. A typical reaction procedure is as follows. Into a mixture of $PbBr_2$ (37 mg, 0.1 mmol) and Al foil (32 mg, 1.2 mmol) in DMF (5 mL) was added 2,2,2-trichloro-1-(4-chlorophenyl)ethyl acetate (**3a**) (302 mg, 1.0 mmol), and the mixture was stirred at ambient temperature until most of **3a** was consumed (3.5 h). The reaction was quenched with aqueous 5% hydrochloric acid, and the mixture was extracted with hexane–ether (1:1) (6 mL × 5). The combined extracts were washed with aqueous $NaHCO_3$ (6 mL) and brine (6 mL × 4), dried over Na_2SO_4, and concentrated. The residue was chromatographed on a silica gel column (hexane/EtOAc, 20/1) to give 4-chloro-1-(2,2-dichloroethenyl)benzene (**4a**) (174 mg, 84%) as a colorless liquid. The reaction conditions and results are listed in Table IV (entries 2, 5, 8, 11, and 14).

Reductive Removal of Chlorine Atom from 2. Under similar conditions described for 1,2-elimination of the acetates **3** (method B), reductive removal of chlorine atom from **2** took place to afford **5**. The reaction conditions and results are shown in Table IV (entries 3, 6, 9, 12, and 15).

Identification of Products 2–5. 2,2,2-Trichloro-1-(4-chlorophenyl)ethanol (**2a**),[11] 2,2,2-trichloro-1-phenylethanol (**2b**),[4d] 2,2,2-trichloro-1-(3,4-methylenedioxyphenyl)ethanol (**2c**),[18] 2,2,2-trichloro-1-(2-thienyl)ethanol (**2e**),[19] 1,1,1-trichloro-3-ethylheptan-2-ol (**2f**),[20] 1,1,1-trichloro-4-phenyl-3-buten-2-ol (**2g**),[1d] 1,1,1-trichloro-4-methyl-3-penten-2-ol (**2h**),[21] 2,2,2-trichloro-1-(4-hydroxyphenyl)ethanol (**2i**),[6c] 2,2,2-trichloro-1-(3,4-dihydroxyphenyl)ethanol (**2j**),[22] 2,2,2-tribromo-1-(4-chlorophenyl)ethanol (**2k**),[23] 2,2,2-trichloro-1-(4-chlorophenyl)ethyl acetate (**3a**),[24] 2,2,2-trichloro-1-phenylethyl acetate (**3b**),[25] 2,2,2-trichloro-1-(3,4-methylenedioxyphenyl)ethyl acetate (**3c**),[26] 2,2,2-trichloro-1-styrylethyl acetate (**3g**),[27] 4-chloro-1-(2,2-dichloroethenyl)benzene (**4a**),[28] (2,2-dichloroethenyl)benzene (**4b**),[29] 1-(2,2-dichloroethenyl)-3,4-(methylenedioxy)benzene (**4c**),[24] 1,1-dichloro-3-ethyl-1-heptene (**4f**),[30] 1,1-dichloro-4-phenylbutadiene (**4g**),[31] 1-(2,2-dichloroethenyl)-4-hydroxybenzene (**4i**),[32] 2,2-dichloro-1-(4-chlorophenyl)ethanol (**5a**),[33] 2,2-dichloro-1-phenylethanol (**5b**),[34] 1,1-dichloro-3-ethyl-2-heptanol (**5f**),[35] and 1,1-dichloro-4-phenyl-3-buten-2-ol (**5g**)[34] were identified by comparison of their spectral data with those described in the references or with authentic samples. The other products were confirmed by spectroscopic and elemental analyses as shown below.

2,2,2-Trichloro-1-(3-indolyl)ethanol (2d): IR ($CHCl_3$) 3560 (OH), 3450 (NH), 3050, 1550 (C=C), 1455, 1420, 1340, 1030, 907, 825 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.48 (br s, 1 H, OH), 5.36 (s, 1 H, CHO), 6.90–7.40 (m, 4 H, Ar), 7.50–7.77 (m, 1 H, CH=C), 8.04 (br s, 1 H, NH). Anal. Calcd for $C_{10}H_8Cl_3NO$: C, 45.40; H, 3.05; N, 5.29. Found: C, 45.43; H, 2.76; N, 5.00.

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2-Carbamoyl-2,2-dichloro-1-(4-chlorophenyl)ethanol (2m): mp 112–114 °C; IR (Nujol) 3340, 3290, 3230, 3170, 1690 (C=O), 1460, 1375, 1105, 835, 822 cm^{-1}; ^1H NMR (acetone-d_6) δ 3.62 (br s, 1 H, OH), 4.58 (s, 1 H, CHO), 7.23 (s, 4 H, Ar), 7.40 (br s, 2 H, NH_2). Anal. Calcd for $C_9H_8Cl_3NO_2$: C, 40.26; H, 3.00; N, 5.22. Found: C, 40.30; H, 2.80; N, 5.02.

2,2-Dichloro-1-(4-chlorophenyl)-2-cyanoethanol (2n): IR (CCl_4) 3440 (OH), 1595 (C=C), 1492 (C=C), 1185, 1093, 1014, 850, 820 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.67 (br s, 1 H, OH), 5.00 (s, 1 H, CHO), 7.16–7.50 (m, 4 H, Ar). Anal. Calcd for $C_9H_6Cl_3NO$: C, 43.15; H, 2.41; N, 5.59. Found: C, 43.18; H, 2.20; N, 5.47.

2,2-Dichloro-1-(4-chlorophenyl)-2-(ethoxycarbonyl)-ethanol (2o): IR (neat) 3460 (OH), 1730 (C=O), 1600 (C=C), 1495 (C=C), 1240, 1087, 1053, 1012, 865, 830 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.28 (t, J = 7 Hz, 3 H, CH_3), 3.40 (br s, 1 H, OH), 4.25 (q, J = 7 Hz, 2 H, CH_2O), 6.03 (s, 1 H, CHO), 7.27 (s, 4 H, Ar). Anal. Calcd for $C_{11}H_{11}Cl_3O_3$: C, 44.40; H, 3.73. Found: C, 44.42; H, 3.61.

1,1,1-Trichloro-3-ethylhept-2-yl acetate (3f): IR (neat) 1760 (C=O), 1455, 1367, 1210, 1025, 800, 780, 758 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.65–2.34 (m, 15 H, CH_3, CH_2, CH), 2.14 (s, 3 H, CH_3CO), 5.40 (d, J = 2 Hz, 1 H, CHO). Anal. Calcd for $C_{11}H_{19}Cl_3O_2$: C, 45.62; H, 6.61. Found: C, 45.50; H, 6.70.

2,2-Dichloro-1-(3,4-(methylenedioxy)phenyl)ethanol (5c): IR (neat) 3450 (OH), 3000, 1610 (C=C), 1502 (C=C), 1490, 1447, 1095, 1040, 795, 780, 745 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.98 (br s, 1 H, OH), 4.80 (d, J = 5.2 Hz, 1 H, CHO), 5.67 (d, J = 5.2 Hz, 1 H, $CHCl_2$), 5.89 (s, 2 H, OCH_2O), 6.70–6.95 (m, 3 H, Ar); HRMS calcd for $C_9H_8Cl_2O_3$ m/z 233.9851, found 233.9869.

Ethyl 2-Chloro-3-(4-chlorophenyl)-3-hydroxypropionate (5o): IR (neat) 3480 (OH), 1740 (C=O), 1595 (C=C), 1490 (C=C), 1085, 1010, 850, 820, 713, 703 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.32 (t, J = 7 Hz, 3 H, CH_3), 1.32 (br s, 1 H, OH), 3.54 (d, J = 5 Hz, 1 H, CHCl), 4.27 (q, J = 7 Hz, 2 H, CH_2O), 5.33 (d, J = 5 Hz, 1 H, CHO), 7.11–7.52 (m, 4 H, Ar). Anal. Calcd for $C_{11}H_{12}Cl_2O_3$: C, 50.21; H, 4.60. Found: C, 50.27; H, 4.43.

Ethyl *trans*- and *cis*-3-Formyl-2,2-dimethylcyclopropanecarboxylate (6 and 6′). Ozonolysis of ethyl chrysanthemate according to the method described in the literature[36] gave a mixture of **6** and **6′** in 80% yield. The isomers were separated by column chromatography (SiO_2, hexane/EtOAc, 20/1). The spectral data of **6** and **6′** were fully consistent with the reported data.[17]

Ethyl *trans*-3-(1-Hydroxy-2,2,2-trichloroethyl)-2,2-dimethylcyclopropanecarboxylates (7a). Into a mixture of $PbBr_2$ (37 mg, 0.1 mmol) and finely cut Al foil (40 mg, 1.5 mmol) in DMF (5 mL) were added aldehyde **6** (170 mg, 1.0 mmol) and tetrachloromethane (0.39 mL, 4 mmol), and the mixture was stirred at ambient temperature until most of **6** was consumed (7 h). Aqueous 5% hydrochloric acid (6 mL) was added, and the mixture was extracted with hexane–ether (1:1) (6 mL × 5). The combined extracts were washed with aqueous $NaHCO_3$ (6 mL) and brine (6 mL × 4), dried over Na_2SO_4, and concentrated. The residue was chromatographed on a silica gel column (hexane/EtOAc, 5/1) to give **7a**[37] (252 mg, 87%). The product **7a** was a 1:1 mixture of *dl* and meso isomers: IR ($CHCl_3$) 3570 (OH), 1715 (C=O), 1378, 1172 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.13–1.38 (m, 9 H, CH_3), 1.64–2.07 (m, 2 H, CH), 3.34–3.90 (m, 2 H, OH, CHO), 4.12 (q, J = 7.4 Hz, 2 H, CH_2O); ^{13}C NMR (25.05 MHz, $CDCl_3$) δ 14.3 (q), 19.9 (q), 20.5 (q), 21.9 (q), 22.5 (q), 26.0 (s), 28.8 (s), 30.4 (d), 33.0 (d), 34.5 (d), 34.6 (d), 60.5 (t), 60.8 (t), 81.0 (d), 83.0 (d), 102.9 (s), 103.2 (s), 170.5 (s), 171.4 (s). Anal. Calcd for $C_{10}H_{15}Cl_3O_3$: C, 41.48; H, 5.22. Found: C, 41.55; H, 5.00.

Ethyl *trans*-3-(1-Acetoxy-2,2,2-trichloroethyl)-2,2-dimethylcyclopropanecarboxylate (8a). The compound **7a** (290 mg, 1.0 mmol) was treated with pyridine (0.10 mL, 1.2 mmol) and Ac_2O (2 mL) at ambient temperature for 20 h. The reaction was quenched with aqueous 5% hydrochloric acid, and the mixture was extracted with hexane–ether (1:1) (6 mL × 5). The combined extracts were washed with aqueous $NaHCO_3$ (6 mL × 3) and brine (6 mL × 2), dried over Na_2SO_4, and concentrated. The residue was chromatographed on a silica gel column (hexane/EtOAc, 20/1) to give the corresponding acetate **8a** (305 mg, 92%) as a colorless liquid: IR (neat) 1762 (C=O), 1723 (C=O), 1370, 1115, 1028, 800 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.18 (s, 3 H, CH_3), 1.25 (s, 3 H, CH_3), 1.25 (t, J = 6.8 Hz, 3 H, CH_3), 1.54–2.08 (m, 2 H, CH), 2.16 (s, 3 H, CH_3CO), 4.12 (q, J = 6.8 Hz, 2 H, CH_2), 5.12–5.37 (m, 1 H, CHO); ^{13}C NMR (25.05 MHz, $CDCl_3$) δ 14.3 (q), 19.8 (q), 20.9 (q), 22.4 (q), 22.8 (q), 26.3 (s), 29.6 (s), 30.3 (d), 32.3 (d), 33.4 (d), 34.6 (d), 60.7 (t), 79.7 (d), 80.5 (d), 98.8 (s), 99.8 (s), 168.7 (s), 169.6 (s), 170.3 (s), 170.8 (s). Anal. Calcd for $C_{12}H_{17}Cl_3O_4$: C, 43.46; H, 5.17. Found: C, 43.40; H, 5.04.

Ethyl *trans*-3-(2,2-Dichloroethenyl)-2,2-dimethylcyclopropanecarboxylates (9a). A mixture of acetate **8a** (166 mg, 0.5 mmol), $PbBr_2$ (18 mg, 0.05 mmol), and Al foil (18 mg, 0.65 mmol) in DMF (3 mL) was stirred at ambient temperature for 10 h. Aqueous 5% hydrochloric acid was added, and the mixture was extracted with hexane–ether (1:1) (6 mL × 5). The combined extracts were washed with aqueous $NaHCO_3$ (6 mL) and brine (6 mL × 4), dried over Na_2SO_4, and concentrated. The residue was chromatographed on a silica gel column (hexane/EtOAc, 20/1) to give **9a** (97 mg, 82%) as a colorless liquid. The following spectral data of **9a** were fully consistent with the reported data:[17] IR (neat) 3040, 1725 (C=O), 1615 (C=C), 1220, 1170, 1110, 885, 855 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.17 (s, 3 H, CH_3), 1.27 (s, 3 H, CH_3), 1.27 (t, J = 7.0 Hz, 3 H, CH_3), 1.57 (d, J = 5.4 Hz, 1 H, CH), 2.21 (dd, J = 8.6, 5.4 Hz, 1 H, CH), 4.11 (q, J = 7.0 Hz, 2 H, CH_2O), 5.58 (d, J = 8.6 Hz, 1 H, CH=C); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.3 (q), 20.0 (q), 22.6 (q), 28.8 (s), 32.7 (d), 34.8 (d), 60.6 (t), 121.8 (d), 127.1 (s), 171.1 (s).

Alternatively, direct transformation of **7a** to **9a** was performed as follows. A mixture of **7a** (30 mg, 0.1 mmol), $PbBr_2$ (18 mg, 0.05 mmol), Al foil (14 mg, 0.5 mmol), and 97% sulfuric acid (50 mg, 0.5 mmol) in ethanol (3 mL) was heated at 50–60 °C for 12 h. The reaction mixture was poured into ice-cold water (ca. 10 mL) and extracted with hexane–ether (1:1) (6 mL × 3). The combined extracts were washed with aqueous $NaHCO_3$ (6 mL) and brine (6 mL), dried over Na_2SO_4, and concentrated. The residue was chromatographed on a silica gel column (hexane/EtOAc, 20/1) to give **9a** (19 mg, 78%), whose IR and NMR spectra were fully consistent with those of **9a** obtained above.

Ethyl *trans*-3-(1-Hydroxy-2,2,2-tribromoethyl)-2,2-dimethylcyclopropanecarboxylates (7b). A mixture of tetrabromomethane (497 mg, 1.5 mmol), aldehyde **6** (170 mg, 1.0 mmol), $PbBr_2$ (37 mg, 0.1 mmol), and Al foil (40 mg, 1.5 mmol) in DMF (5 mL) was stirred at ambient temperature (30 h). Workup of the mixture in a similar manner as described above afforded the corresponding product **7b**[37] (169 mg, 40%) as a mixture of two diastereomers together with the recovered **6** (28%).[38] Compound **7b**: IR ($CHCl_3$) 3550 (OH), 1715 (C=O), 1375, 1170, 1110 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.10–1.45 (m, 9 H, CH_3), 1.60–2.05 (m, 2 H, CH), 3.30–3.90 (m, 2 H, OH, CHO), 4.12 (q, J = 7.0 Hz, 2 H, CH_2O). Anal. Calcd for $C_{10}H_{15}Br_3O_3$: C, 28.40; H, 3.57. Found: C, 28.52; H, 3.79.

Ethyl *trans*-3-(1-Acetoxy-2,2,2-tribromoethyl)-2,2-dimethylcyclopropanecarboxylate (8b). The compound **7b** (423 mg, 1.0 mmol) was treated with pyridine (0.10 mL, 1.2 mmol) and Ac_2O (2 mL) at ambient temperature for 20 h to afford **8b** (428 mg, 92%): IR (CCl_4) 1758 (C=O); 1725 (C=O), 1370, 1210, 1175, 1023 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.12–1.54 (m, 9 H, CH_3), 1.54–2.12 (m, 2 H, CH), 2.18 (s, 3 H, CH_3CO), 4.13 (q, J = 7.0 Hz, 2 H, CH_2O), 5.02–5.37 (m, 1 H, CHO). Anal. Calcd for $C_{12}H_{17}Br_3O_4$: C, 31.00; H, 3.69. Found: C, 31.06; H, 3.40.

Ethyl *trans*-3-(2,2-Dibromoethenyl)-2,2-dimethylcyclopropanecarboxylates (9b). A mixture of acetate **8b** (232 mg, 0.5 mmol), $PbBr_2$ (18 mg, 0.05 mmol), and Al foil (18 mg, 0.65 mmol) in DMF (3 mL) was stirred at ambient temperature for 10 h. Workup of the mixture afforded **9b**[39] (235 mg, 72%) as a colorless liquid: IR (neat) 1725 (C=O), 1615 (C=C), 1220, 1173, 1115, 800 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.18 (s, 3 H, CH_3), 1.26 (t, J = 7.0 Hz, 3 H, CH_3), 1.27 (s, 3 H, CH_3), 1.53 (d, J = 5.4 Hz, 1 H, CH), 2.16 (dd, J = 7.6, 5.4 Hz, 1 H, CH), 4.12 (q, J = 7.0 Hz, 2 H, CH_2O), 6.11 (d, J = 7.6 Hz, 1 H, CH=C); ^{13}C NMR (126 MHz,

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(38) Attempts to improve the yield of **7b**, e.g., using excess $PbBr_2$ (0.3 equiv) or Al (>2 equiv), or at higher temperature (50–60 °C), failed.
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$CDCl_3$) δ 14.3 (q), 20.0 (q), 22.7 (q), 28.8 (s), 34.7 (d), 35.8 (d), 60.6 (t), 132.1 (d), 135.7 (s), 171.0 (s).

Ethyl *cis*-3-(1-Hydroxy-2,2,2-trichloroethyl)-2,2-dimethylcyclopropanecarboxylates (7a'). Similarly, reductive addition of tetrachloromethane (4 mmol) to aldehyde **6'** (1 mmol) with $PbBr_2$ (0.1 mmol) and Al foil (3 mmol) in DMF (5 mL) at ambient temperature for 10 h afforded **7a'** (133 mg, 46%) as a mixture of two diastereomers (ca. 7/3) along with lactone **10** (34 mg, 14%). Compound **7a'**:[37] IR ($CHCl_3$) 3570 (OH), 1705 (C=O), 1380, 1180 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.10–1.45 (m, 9 H, CH_3), 1.48–1.90 (m, 2 H, CH), 3.10 (d, J = 6.0 Hz, 0.3 H, OH), 3.67 (d, J = 6.0 Hz, 0.7 H, OH), 3.87–4.35 (m, 2 H, CH_2O), 4.35–4.95 (m, 1 H, CHO). Anal. Calcd for $C_{10}H_{15}Cl_3O_3$: C, 41.48; H, 5.22. Found: C, 41.59; H, 5.37. Lactone **10**:[40] IR (neat) 3070, 1780 (C=O), 1160, 1005, 895, 825, 795, 740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.24 (s, 6 H, CH_3), 2.13 (d, J = 6.0 Hz, 1 H, CH), 2.35 (d, J = 6.0 Hz, 1 H, CH), 4.55 (s, 1 H, CHO).

Ethyl *cis*-3-(1-Acetoxy-2,2,2-trichloroethyl)-2,2-dimethylcyclopropanecarboxylate (8a'). Similarly, acetylation of **7a'** (1.0 mmol) with pyridine (1.2 mmol) and Ac_2O (2 mL) at ambient temperature for 20 h afforded the corresponding acetate **8a'** (97%), whose TLC analysis (hexane/EtOAc, 5/1) showed two spots at R_f 0.44 and 0.36. Each fraction was isolated by column chromatography on silica gel (hexane/EtOAc, 20/1): the less polar fraction (R_f 0.44)/the more polar fraction (R_f 0.36), 4/6. The less polar fraction: IR (neat) 1770 (C=O), 1725 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.19 (s, 6 H, CH_3), 1.19 (t, J = 7.0 Hz, 3 H, CH_3), 1.50–1.87 (m, 2 H, CH), 2.10 (s, 3 H, CH_3CO), 4.07 (q, J = 7.0 Hz, 2 H, CH_2), 6.07–6.46 (m, 1 H, CHO). Anal. Calcd for $C_{12}H_{17}Cl_3O_4$: C, 43.46; H, 5.17. Found: C, 43.51; H, 5.33. The more polar fraction: IR (neat) 1770 (C=O), 1725 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.22 (s, 3 H, CH_3), 1.23 (t, J = 7.0 Hz, 3 H, CH_3), 1.38 (s, 3 H, CH_3), 1.66–1.82 (m, 2 H, CH), 2.03 (s, 3 H, CH_3CO), 4.05 (q, J = 7.0 Hz, 2 H, CH_2O), 5.52–5.90 (m, 1 H, CHO). Anal. Calcd for $C_{12}H_{17}Cl_3O_4$: C, 43.46; H, 5.17. Found: C, 43.56; H, 5.39.

Ethyl *cis*-3-(2,2-Dichloroethenyl)-2,2-dimethylcyclopropanecarboxylates (9a'). Reaction of the acetate **8a'** (0.5 mmol) with $PbBr_2$ (0.1 mmol) and Al foil (1.5 mmol) in DMF (3 ml) at 50–60 °C for 24 h afforded **9a'** (80%) as a colorless liquid. The following spectral data of **9a'** were fully consistent with the reported data:[16e,17] IR (neat) 3060, 1725 (C=O), 1615 (C=C), 1195, 1140, 920, 810 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.23 (s, 6 H, CH_3), 1.25 (t, J = 7.0 Hz, 3 H, CH_3), 1.78 (d, J = 8.0 Hz, 1 H, CH), 2.01 (t, J = 8.0 Hz, 1 H, CH), 4.08 (q, J = 7.0 Hz, 2 H, CH_2O), 6.20 (d, J = 8.0 Hz, 1 H, CH=C); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.3 (q), 14.9 (q), 27.3 (q), 28.4 (s), 31.9 (d), 32.4 (d), 60.3 (t), 120.4 (d), 125.0 (s), 170.6 (s).

Ethyl *cis*-3-(1-Hydroxy-2,2,2-tribromoethyl)-2,2-dimethylcyclopropanecarboxylate (7b'). Reaction of tetrabromomethane (4 mmol) and **6'** (1 mmol) with $PbBr_2$ (0.1 mmol) and Al foil (3 mmol) in DMF (5 mL) at ambient temperature for 30 h afforded **7b'**[37] (42%) as a mixture of two diastereomers: IR (neat) 3430 (OH), 1720 (C=O), 1380 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.10–1.48 (m, 9 H, CH_3), 1.50–1.93 (m, 2 H, CH), 3.30 (br s, 1 H, OH), 3.93–4.36 (m, 2 H, CH_2O), 4.75 (diffused d, J = 8.6 Hz, 1 H, CHO). Anal. Calcd for $C_{10}H_{15}Br_3O_3$: C, 28.40; H, 3.57. Found: C, 28.26; H, 3.83.

Ethyl *cis*-3-(1-Acetoxy-2,2,2-tribromoethyl)-2,2-dimethylcyclopropanecarboxylate (8b'). Acetylation of **7b'** afforded the corresponding acetate **8b'** (85%) as a mixture of two diastereomers, whose column chromatography on silica gel (hexane/EtOAc, 20/1) gave the less polar fraction (R_f 0.39) and the more polar fraction (R_f 0.32) in a ratio of 6/4. The less polar fraction: IR (neat) 1760 (C=O), 1720 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.24 (s, 6 H, CH_3), 1.24 (t, J = 7.0 Hz, 3 H, CH_3), 1.63–2.08 (m, 2 H, CH), 2.15 (s, 3 H, CH_3CO), 4.12 (q, J = 7.0 Hz, 2 H, CH_2O), 6.24 (d, J = 8.4 Hz, 1 H, CHO). Anal. Calcd for $C_{12}H_{17}Br_3O_4$: C, 31.00; H, 3.69. Found: C, 30.88; H, 3.79. The more polar fraction: IR (neat) 1760 (C=O), 1720 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.23 (s, 3 H, CH_3), 1.23 (t, J = 7.0 Hz, 3 H, CH_3), 1.44 (s, 3 H, CH_3), 1.63–1.90 (m, 2 H, CH), 2.04 (s, 3 H, CH_3CO), 4.04 (q, J = 7.0 Hz, 2 H, CH_2O), 5.55 (dd, J = 6.6, 3.6 Hz, 1 H, CHO). Anal. Calcd for $C_{12}H_{17}Br_3O_4$: C, 31.00; H, 3.69. Found: C, 30.84; H, 3.87.

Ethyl *cis*-3-(2,2-Dibromoethenyl)-2,2-dimethylcyclopropanecarboxylates (9b'). Reaction of the acetate **8b'** (0.5 mmol) with $PbBr_2$ (0.1 mmol) and Al foil (1.5 mmol) in DMF (3 mL) at 50–60 °C for 24 h afforded **9b'**[16e] (81%) as a colorless liquid: IR (neat) 3040, 1720 (C=O), 1610 (C=C), 1135, 765 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.24 (s, 6 H, CH_3), 1.24 (t, J = 7.0 Hz, 3 H, CH_3), 1.58–1.97 (m, 2 H, CH), 4.08 (q, J = 7.0 Hz, 2 H, CH_2O), 6.73 (dd, J = 6.8, 2.0 Hz, 1 H, CH=C); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.3 (q), 14.9 (q), 27.3 (q), 28.4 (s), 31.9 (d), 32.4 (d), 60.3 (t), 120.4 (d), 125.0 (s), 170.6 (s).

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(40) The lactone **10** has been found to be converted to **9a'** in almost quantitative yield: Kondo, K.; Takashima, T.; Tunemoto, D. *Chem. Lett.* **1979**, 1185.