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Reaction of α,β-Unsaturated Carboxylic Acids with Manganese(III) Acetate in the Presence of Chloride Ion

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The reaction of 3-phenylpropenoic acids with manganese(III) acetate-Cl^- complex yielded 1,2,2-trichloro-1-phenylethanes, 1-acetoxy-2,2-dichloro-1-phenylethanes, and 2,2-dichloro-1-phenylethanols. (*E*)-2,3-Diphenylpropenoic acids gave 2,2-dichloro-1,2-diphenylethanones and 2-acetoxy-1,2-diphenylethanones. 3,3-Diphenylpropenoic acids yielded 2,2-dichloro-1,1-diphenylethenes, 1-acetoxy-2,2-dichloro-1,1-diphenylethanes, 2,2-dichloro-1,1-diphenyl-1-ethanols, and 2-hydroxy-2,2-diphenylethanal. Fluorenylideneacetic acid gave 9-chloro-9-(dichloromethyl)fluorene, 9-acetoxy-9-(dichloromethyl)fluorene, and 9-fluorenone. 1-Cyclohexenecarboxylic acid yielded 1,2-dichlorocyclohexanecarboxylic acid and 1-acetoxy-2-chlorocyclohexanecarboxylic acid. The reaction can be explained in terms of a free-radical mechanism involving manganese(III) acetate-Cl^- complexation, addition of $Cl^\bullet$ radical, decarboxylation, and the oxidation of chloroethenes which are the reaction intermediates.

Although there are many investigations into the reaction of manganese(III) acetate,[1] the reaction of manganese(III) acetate in the presence of Cl^- ion which forms a complex[2] has not been fully examined. The reaction of aromatic compounds with this complex gave chlorine-substituted products,[3] while olefins yielded mainly addition products.[2,3] In a previous paper[4] we have reported that the reaction of aryl ketones with manganese(III) acetate–LiCl gave α-chlorinated ketones in good yield. We have examined the reactions of α,β-unsaturated carboxylic acids, such as 3-phenylpropenoic acids, (*E*)-2,3-diphenylpropenoic acids, 3,3-diphenylpropenoic acids, fluorenylideneacetic acid, and 1-cyclohexenecarboxylic acid with the complex. These acids were chosen for the reason that they may provide a variety of products which reflect the nature of the reaction and that the products will be easily characterized by spectrometry. The reactions of these acids yielded chlorine addition and substitution products accompanied by decarboxylation. We will describe these reactions and the possible mechanisms in this paper.

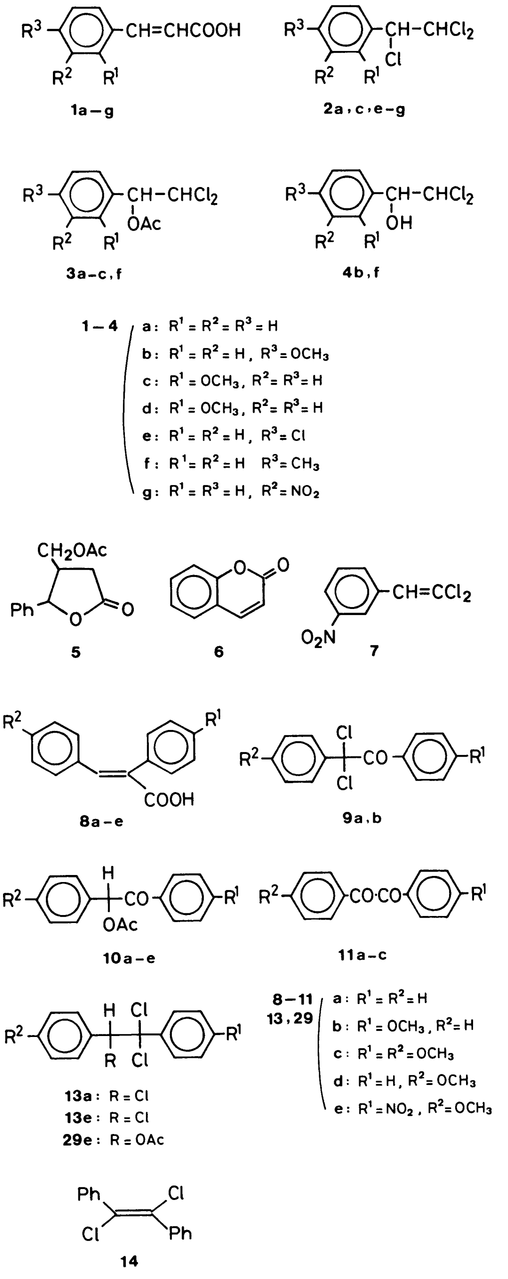
Results and Discussion

3-Phenylpropenoic Acids (1a—g). When a mixture of (*E*)-3-phenylpropenoic aicd (**1a**), manganese(III) acetate[5,6] and LiCl in a molar ratio of 1:10:20 in AcOH was heated under reflux, it gave 1,2,2-trichloro-1-phenylethane (**2a**) and 1-acetoxy-2,2-dichloro-1-phenylethane (**3a**). The reaction was conducted at various molar ratios of manganese(III) acetate and LiCl, and the yields changed with changing the amounts of manganese(III) acetate and LiCl (Table 1,

Table 1. The Oxidations of 3-Phenylpropenoic Acids (**1a—g**) and 1-Chloro-2-phenylethene (**26a**) with Manganese(III) Acetate in the Presence of Chloride Ion at the Reflux Temperature

Entry	Substrate	Molar ratio[a]	Salt	Reaction time/min	Product (yield/%)[b]		
1	**1a**	1 : 5 : 10	LiCl	170	**2a**(28)		
2	**1a**	1 : 8 : 10	LiCl	310	**2a**(48)		
3	**1a**	1 : 10 : 10	LiCl	300	**2a**(40)		
4	**1a**	1 : 10 : 15	LiCl	350	**2a**(51)		
5	**1a**	1 : 10 : 20	LiCl	410	**2a**(45)	**3a**(6)	
6	**1a**	1 : 10 : 20[c]	LiCl	310	**2a**(49)	**3a**(3)	
7	**1a**	1 : 10 : 30	LiCl	340	**2a**(36)	**3a**(5)	
8	**1a**	1 : 10 : 7.5	$CaCl_2$	570	**2a**(54)	**3a**(4)	
9	**1a**	1 : 10 : 15	NH_4Cl	660	**2a**(27)		
10	**1a**	1 : 10 : 5	$AlCl_3$	30	**2a**(15)	**3a**(6)	
11	**1a**	1 : 10 : 15	NaCl	300	**2a**(10)		**5** (6)
12	**1a**	1 : 10 : 15	HCl	510	**2a**(7)		**5** (16)
13	**1a**	1 : 8 : 10	KCl	210	**2a**(15)		**5** (6)
14	**1b**	1 : 8 : 16	LiCl	340		**3b**(54)	**4b**(17)
15	**1c**	1 : 8 : 16	LiCl	150	**2c**(11)	**3c**(52)	
16	**1d**	1 : 8 : 16	LiCl	240	**2c**(8)	**3c**(42)	**6** (30)
17	**1e**	1 : 8 : 16	LiCl	410	**2e**(58)[d]		
18	**1f**	1 : 8 : 16	LiCl	400	**2f**(51)	**3f**(19)	**4f**(4)[e]
19	**1g**	1 : 10 : 15	LiCl	340	**2g**(35)		**7** (7)[f]
20	**26a**	1 : 4 : 12	LiCl	250	**2a**(51)	**3a**(6)	

a) Substrate:Manganese(III) acetate:Salt. b) Isolated yields based on the substrate added. c) Ac_2O (20 equivalents) was added. d) **1e** was recovered (5%). e) 4-Methylbenzoic acid was obtained (13%). f) **1g** was recovered (40%).



Entries 1—5, 7). Addition of Ac_2O to the reaction mixture caused no appreciable change in the yield, but shortened the reaction time considerably (Entry 6). It was observed that changing the Cl^- ion source affected the yield and $CaCl_2$ was as good as LiCl, but it took a longer reaction time. In the reactions using NaCl, HCl, or KCl, 4-acetoxymethyl-5-phenyl-4-butanolide (**5**) was isolated. Hereafter we employed LiCl as the Cl^- ion source. Then the reactions of (*E*)-3-(4-methoxyphenyl)- (**1b**), (*E*)-3-(2-methoxyphenyl)- (**1c**), (*Z*)-3-(2-methoxyphenyl)- (**1d**), (*E*)-3-(4-chlorophenyl)- (**1e**), (*E*)-3-(4-methylphenyl)- (**1f**), and (*E*)-3-(3-nitrophenyl)propenoic acid (**1g**) were examined. The structures of the products were determined by studying their ¹H NMR, IR, mass spectra and elemental analyses. A summary of the reaction conditions and the yields of the products are presented in Table 1.

(*E*)-2,3-Diphenylpropenoic Acids (8a—d). The reaction of (*E*)-2,3-diphenylpropenoic acid (**8a**) with manganese(III) acetate-Cl^- complex gave 2,2-dichloro-1,2-diphenylethanone (**9a**), 2-acetoxy-1,2-diphenylethanone (**10a**), 1,2-diphenylethanedione (**11a**), benzoic acid (**12**), 1,1,2-trichloro-1,2-diphenylethane (**13a**) and (*E*)-1,2-dichloro-1,2-diphenylethene (**14**). The reaction of (*E*)-2-(4-methoxyphenyl)-3-phenylpropenoic acid (**8b**) yielded the corresponding ethanones (**9b** and **10b**) and an ethanedione (**11b**). The reactions of (*E*)-2,3-bis(4-methoxyphenyl)propenoic acid (**8c**) and (*E*)-3-(4-methoxyphenyl)-2-phenylpropenoic acid (**8d**) yielded no chlorinated compounds, but gave 2-acetoxy-1,2-diphenylethanones (**10c** and **10d**) and 1,2-diphenylethanediones (**11b** and **11c**) (Table 2). It should be pointed out that the carbonyl carbon in the ethanones is assigned by ¹H NMR to the carbon on which the carboxyl group of the acid had been located and that the acetoxyl group is introduced more readily to the carbon attached to a methoxyphenyl group than to a phenyl group.

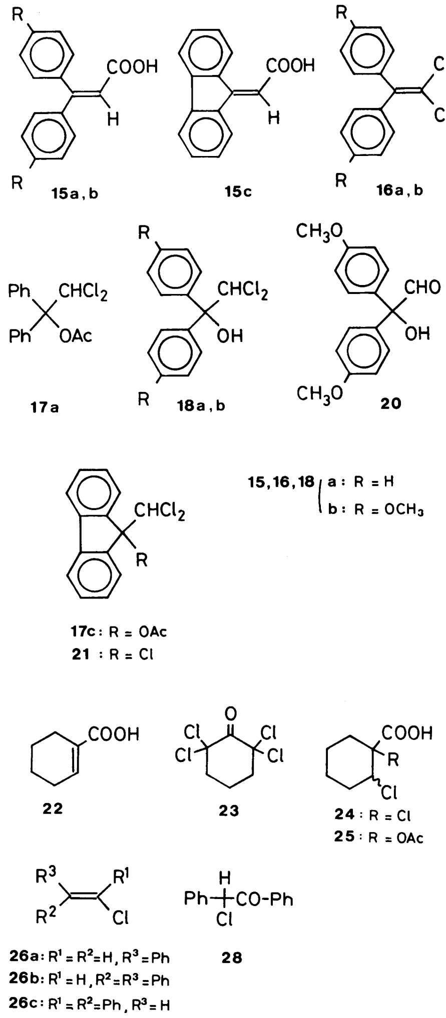


Fig. 1.

3,3-Diphenylpropenoic Acids (15a,b) and Fluorenylideneacetic Acid (15c). When 3,3-diphenylpropenoic

Table 2. The Oxidations of (*E*)-2,3-Diphenylpropenoic Acids (**8a**—**d**) and 1-Chloro-1,2-diphenylethene (**26c**) with Manganese(III) Acetate in the Presence of LiCl at the Reflux Temperature

Substrate	Molar ratio[a]	Reaction time/min	Product (yield/%)[b]				
8a	1 : 6 : 12	40	**9a**(50)	**10a**(6)	**11a**(13)	**13a**(5)	**14**(5)[c]
8b	1 : 6 : 12	116	**9b**(32)	**10b**(22)	**11b**(28)		
8c	1 : 6 : 12	160		**10c**(78)	**11c**(19)		
8d	1 : 6 : 12	120		**10d**(73)	**11b**(18)		
26c	1 : 4 : 12	80	**9a**(25)		**11a**(6)	**13a**(14)	**14**(17)

a) Substrate:Manganese(III) acetate:LiCl. b) Isolated yields based on the substrate added. c) Benzoic acid was obtained (9%).

Table 3. The Oxidation of 3,3-Diphenylpropenoic Acids (**15a**, **b**), Fluorenylideneacetic Acid (**15c**) and 2-Chloro-1,1-diphenylethene (**26b**) with Manganese(III) Acetate in the Presence of LiCl at the Reflux Temperature

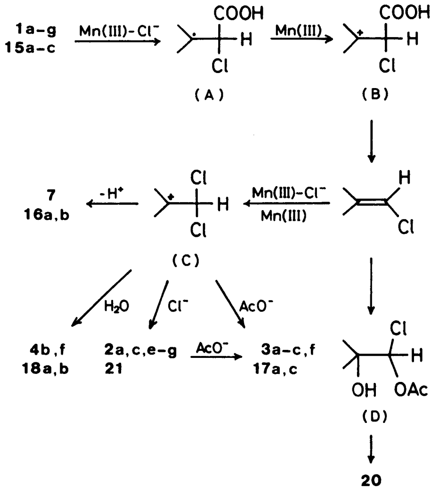
Substrate	Molar ratio[a]	Reaction time/min	Product (yield/%)[b]			
15a	1 : 10 : 15	480	**16a**(9)	**17a**(42)	**18a**(40)	**19a**(4)
15a	1 : 10 : 15[c]	420	**16a**(10)	**17a**(72)		
15b	1 : 4 : 8	1	**16b**(46)		**18b**(3)	**20** (8)
15c	1 : 6 : 18	230		**17c**(37)	**19c**(12)	**21** (49)
26b	1 : 4 : 12	330	**16a**(20)	**17a**(41)	**18a**(35)	

a) Substrate:Manganese(III) acetate:LiCl. b) Isolated yields based on the substrate added. c) Ac_2O (15 equivalents) was added.

acid (**15a**) was oxidized with manganese(III) acetate-Cl^- complex in AcOH, 2,2-dichloro-1,1-diphenylethene (**16a**) and 1-acetoxy-2,2-dichloro-1,1-diphenylethane (**17a**), 2,2-dichloro-1,1-diphenylethanol (**18a**) and benzophenone (**19a**) were obtained. A remarkable change has been observed when Ac_2O was added to the reaction mixture, i.e. **17a** became the major product (Table 3). The reaction of 3,3-bis(4-methoxyphenyl)-propenoic acid (**15b**) with the complex in a molar ratio of 1:4:8 ended in extremely short reaction time, giving 2,2-dichloro-1,1-bis(4-methoxyphenyl)ethene (**16b**), 2,2-dichloro-1,1-bis(4-methoxyphenyl)ethanol (**18b**), and 2-hydroxy-2,2-bis(4-methoxyphenyl)ethanal (**20**). The reaction of fluorenylideneacetic acid (**15c**) yielded 9-acetoxy-9-(dichloromethyl)fluorene (**17c**), 9-fluorenone (**19c**), and 9-chloro-9-(dichloromethyl)fluorene (**21**).

1-Cyclohexenecarboxylic Acid (22). The reaction of **22** gave 2,2,6,6-tetrachlorocyclohexanone (**23**) (7%), 1,2-dichlorocyclohexanecarboxylic acid (**24**) (17%), and 1-acetoxy-2-chlorocyclohexanecarboxylic acid (**25**) (24%). These acids were separated and identified after methylation with diazomethane. The configuration of these acids could not be determined.

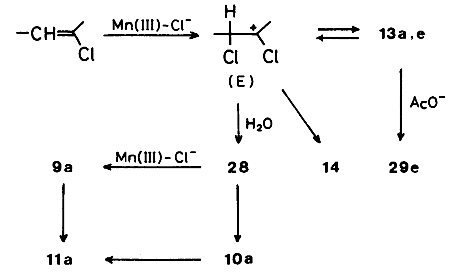
The reactions of 3-phenyl- and 3,3-diphenylpropenoic acids with manganese(III) acetate-Cl^- complex yielded chlorine-substituted ethenes and ethanes. By contrast, 2,3-diphenylpropenoic acids yielded 2,2-dichloro-1,2-diphenylethanones and 2-acetoxy-1,2-diphenylethanones. Addition of an acetoxyl group in place of a chlorine atom is often observed in these reactions. As postulated in the reaction of olefins with manganese(III) acetate in the presence of Cl^- ion,[2] the first step in the reaction of the acids must be the formation of a manganese(III) acetate-Cl^- complex which produces a $Cl^\bullet$ radical. The $Cl^\bullet$ radical adds to the C-2 of the substituted propenoic acid, producing a secondary or tertiary carbon radical A which is then oxidized to the corresponding carbonium ion B (Scheme 1). It seems also possible that the acid coordinates to the manganese(III) acetate-Cl^- complex and a chlorine atom is then transferred from the complex to the C-2 of the propenoic acid, forming the radical A. When the carboxyl group is eliminated from B as CO_2, then a chloroethene (**26a,b**) is formed which may react further with manganese(III) acetate-Cl^- complex to give another carbonium ion C. It was confirmed that 2,3-dichloro-3-phenylpropanoic acid (**27**) which could be formed by the addition of chlorine to the $C=C$ bond in **1a**, was only partially decarboxylated and chlorinated under the reaction conditions to give 1,1,2-trichloro-2-phenylethane (**2a**) (17%), suggesting that this route makes only a small contribution for the formation of **2a**. The carbonium ion C gives dichloroethenes, 1,2,2-trichloroethanes, and 1-acetoxy-2,2-dichloroethanes depending on either losing a proton on the adjacent carbon or taking up a Cl^- ion and an acetate ion. If H_2O which may be contained in the reaction mixture attacks C, then alcohols are formed. The fact that the formation of **18a** was suppressed when the reaction of **15a** was conducted under anhydrous conditions (Table 3) confirms this view. In the reactions of **1b**—**d** and **15a**, an acetoxyl group was preferentially introduced onto the carbon bearing two phenyl groups or a methoxyphenyl group. The chlorine atom at the benzylic position could be readily replaced by an acetate ion,[4] and **2c** was transformed into **3c** by heating in AcOH containing manganese(II) acetate. The formation of **10a** and **10b** in the reactions of **8a** and **8b** showed that the nucleophilic attack with acetate ion also takes place at the carbon attached to the phenyl group to a limited extent.



Scheme 1.

Chloroethenes as the postulated intermediates have not been found in the products, probably because they react faster than the original acid with manganese(III) acetate-Cl^- complex. In order to prove the involvement of chloroethenes as the reaction intermediate, 1-chloro-2-phenylethene (**26a**), which was prepared by an alternative method, was oxidized with the complex in AcOH and it did give the identical products with those from **1a** in a similar ratio (Table 1, Entry 20). Similarly, 2-chloro-1,1-diphenylethene (**26b**) was prepared and oxidized with the complex to yield **16a**, **17a**, and **18a** in a ratio similar to that from **15a** (Table 3). The formation of **20** in the reaction of **15b** deserves comment. It seems that because of the electron-donating effect of the two 4-methoxyphenyl groups in **15b**, the corresponding substituted 2-chloroethene, the intermediate, reacts with the complex via an electron-transfer mechanism[7] to give an α-glycol monoacetate (D) which can be hydrolyzed to **20**.

It has been mentioned already that the carbonyl carbon in 1,2-diphenylethanones (**9b** and **10b,d**) was assigned at the carbon on which the carboxyl group had been located. This was indicated by the presence of the characteristic lower field aromatic protons ortho to the carbonyl group of ethanones in their ^{1}H NMR spectra. This leads to a suggestion that the intermediate, 1-chloro-1,2-diphenylethene (**26c**), is converted into a 1,2-dichloro-1,2-diphenyl cation E which is in equilibrium with 1,1,2-trichloro-1,2-diphenylethane (**13a**) and eventually gives rise to 2-chloro-1,2-diphenylethanone (**28**) as shown in Scheme 2. In fact, the reaction of 1-chloro-1,2-diphenylethene (**26c**) gave **9a**, **11a**, **13a**, and **14** (Table 2) and the treatment of **13a** with manganese(II) acetate in AcOH yielded **28** in a 80% yield. For further confirmation of the mechanism for the formation of 2,2-dichloro-1,2-diphenylethanones and 2-acetoxy-1,2-diphenylethanones, the reaction of (*E*)-3-(4-methoxyphenyl)-2-(4-nitrophenyl)propenoic acid (**8e**) with manganese(III) acetate-Cl^- complex was carried out. The corresponding 1,2-dichloro-1,2-diphenylethyl cation E from **8e** may be destabilized by the electron-withdrawing effect of the *p*-nitro group so that the equilibrium lies toward the right in favor of the formation of 1,1,2-trichloro (**13e**) and hence 2-acetoxy-1,1-dichloro derivative (**29e**). Accordingly, the cation E has less chance to form a 2-chloro-1,2-diphenylethanone (**28**). The reaction indeed yielded 2-acetoxy-1,1-dichloro-2-(4-methoxyphenyl)-1-(4-nitrophenyl)ethane (**29e**) as the major product (36%), accompanied with 2-acetoxy-2-(4-methoxyphenyl)-1-(4-nitrophenyl)ethanone (**10e**) (24%), and 1,1,2-trichloro-2-(4-methoxyphenyl)-1-(4-nitrophenyl)ethane (**13e**) (4%). The compound **28** can be either chlorinated to give **9a** or converted to **10a**,[4] and the routes to **11a** from **9a** and **10a** have been established.[8]



Scheme 2.

In the reaction of 1-cyclohexenecarboxylic acid (**22**) the yield of the decarboxylated product, 2,2,6,6-tetrachlorocyclohexanone (**23**), was poor, probably because the corresponding cation B is less stabilized and quickly takes up a chloride ion to form 1,2-dichlorocyclohexanecarboxylic acid (**24**). The compound **25** can be obtained from **24** on treatment with manganese(II) acetate in boiling AcOH.

It is thus concluded that the reaction of aryl-substituted propenoic acids with manganese(III)-Cl^- complex proceeds via chloro-substituted ethenes formed by chlorination and decarboxylation of the acids. Although there are several decarboxylation reactions to form alkyl or aryl halides[9,10] and our reaction is limited only to aryl-substituted propenoic acids, the use of manganese(III) acetate-Cl^- complex as a decarboxylating reagent is a method of choice when chloro-substituted phenylethanes and phenylethenes are needed.

Experimental

Measurements. The IR spectra were measured in chloroform solution on a JASCO A-102 infrared spectrometer. The ^{1}H NMR spectra were recorded on a Hitachi Perkin-Elmer R-24 spectrometer (60 MHz) with tetramethylsilane as an internal standard; the chemical shifts are reported in δ values. The mass spectra were obtained with a JEOL JMS-DX300 and a JEOL JMS-DX303 mass spectrometer. The melting points were determined on a Yanagimoto micromelting point apparatus and were not corrected.

Materials. (*E*)-3-(4-Methoxyphenyl)propenoic acid (**1b**),[11] (*E*)-3-(2-methoxyphenyl)propenoic acid (**1c**),[12] (*Z*)-3-(2-methoxyphenyl)propenoic acid (**1d**),[13] (*E*)-3-(4-methylphenyl)propenoic acid (**1f**),[14] fluorenylideneacetic acid (**15c**),[15] and 1-cyclohexenecarboxylic acid (**22**)[16] were prepared by the method described in the literature. (*E*)-2,3-Diphenylpropenoic acid (**8a**), (*E*)-2-(4-methoxyphenyl)-3-phenylpropenonic acid (**8b**), (*E*)-2,3-bis(4-methoxyphenyl)propenoic acid (**8c**), (*E*)-3-(4-methoxyphenyl)-2-phenylpropenoic acid (**8d**), and (*E*)-3-(4-methoxyphenyl)-2-(4-nitrophenyl)propenoic acid (**8e**) were prepared from the corresponding arylacetic acid and benzaldehyde by Perkin condensation.[11]

(*E*)-2,3-Bis(4-methoxyphenyl)propenoic Acid (8c): Colorless needles; mp 212 °C (subl.); ^{1}H NMR (DMSO-d_6) δ=3.71 (3H, s, OCH$_3$), 3.79 (3H, s, OCH$_3$), 6.6—7.3 (8H, m, ar.H), 7.70 (1H, s, =CH-), and 12.3 (1H, br., COO$\underline{\text{H}}$). Anal. ($C_{17}H_{16}O_4$) C, H.

3,3-Diphenylpropenoic acid (**15a**) and 3,3-bis(4-methoxyphenyl)propenoic acid (**15b**) were prepared from the corresponding benzophenone and ethyl bromoacetate by Reformatsky reaction.[17] (*E*)-3-Phenylpropenoic acid (**1a**), (*E*)-3-(4-chlorophenyl)propenoic acid (**1e**), and (*E*)-3-(3-nitrophenyl)propenoic acid (**1g**) were purchased from Aldrich Chemical Company, Inc. and Wako Pure Chemical Industries, Ltd.

Oxidations of α,β-Unsaturated Carboxylic Acids with Manganese(III) Acetate-Cl$^-$. The general procedure for the oxidation of α,β-unsaturated carboxylic acids with manganese(III) acetate-Cl$^-$ was as follows. To a heated solution of manganese(III) acetate[5] (4—10 mmol) and chloride anion (see Table 1) in AcOH (30 cm^3), a carboxylic acid (1 mmol) was added. The mixture was then heated under reflux until the brown color of the solution had become transparent. After removal of the solvent, 2 M (1 M=1 mol dm^{-3}) hydrochloric acid (40 cm^3) was added to the mixture, which was then extracted with benzene or chloroform (3×30 cm^3). The benzene (or chloroform) solution was washed with aqueous sodium hydrogencarbonate solution and evaporated in vacuo. The products were separated on preparative TLC (Kieselgel 60G or Wakogel B-10), with chloroform or benzene as the developing solvent. The aqueous sodium hydrogencarbonate solution was acidified with concd hydrochloric acid and extracted with either chloroform or ethyl acetate, which gave acidic products. The yields are summarized in Tables 1—3.

Oxidation Products of (*E*)-3-Phenylpropenoic Acid (1a). 1,2,2-Trichloro-1-phenylethane (2a): Bp 190 °C/2400 Pa (bath temperature); the ^{1}H NMR data agreed with those reported.[18]

1-Acetoxy-2,2-dichloro-1-phenylethane (3a): The ^{1}H NMR data agreed with those reported.[19]

4-Acetoxymethyl-5-phenyl-4-butanolide (5): Colorless liquid; bp 175 °C/1.3 Pa (bath temperature); IR 1780 (-COO-), 1755 cm^{-1} (OAc); ^{1}H NMR (CCl$_4$) δ=2.00 (3H, s, OAc), 2.0—3.0 (3H, m,>CHCH$_2$-), 4.17 (2H, d, J=5.4 Hz, -CH$_2$OAc), 5.21 (1H, d, J=6.0 Hz,>CH-O-), 7.32 (5H, m, ar.H). Anal. ($C_{13}H_{14}O_4$) C, H.

Oxidation Products of (*E*)-3-(4-Methoxyphenyl)propenoic Acid (1b). 1-Acetoxy-2,2-dichloro-1-(4-methoxyphenyl)ethane (3b): Colorless liquid; IR 1747 cm^{-1} (OAc); ^{1}H NMR (CCl$_4$) δ=2.04 (3H, s, OAc), 3.66 (3H, s, OCH$_3$), 5.77 (1H, d, J=5.4 Hz, -CHCl$_2$), 5.93 (1H, d, J=5.4 Hz, >CHOAc), 6.76 (2H, m, H-3 and H-5), and 7.24 (2H, m, H-2 and H-6). Found: *m/z* 262.0154. Calcd for $C_{11}H_{12}{}^{35}Cl_2O_3$: M, 262.0164.

2,2-Dichloro-1-(4-methoxyphenyl)ethanol (4b): Colorless liquid; the ^{1}H NMR and IR spectra were identical with those reported.[20]

Oxidation Products of (*E*)-3-(2-Methoxyphenyl)propenoic Acid (1c) and (*Z*)-3-(2-Methoxyphenyl)propenoic Acid (1d). 1,2,2-Trichloro-1-(2-methoxyphenyl)ethane (2c): Colorless liquid; ^{1}H NMR (CCl$_4$) δ=3.84 (3H, s, OCH$_3$), 5.60 (1H, d, J=6.0 Hz, -CHCl$_2$), 6.06 (1H, d, J=6.0 Hz, -CHCl-), and 6.8—7.6 (4H, m, ar.H). Found: *m/z* 237.9735. Calcd for $C_9H_9{}^{35}Cl_3O$: M, 237.9719.

1-Acetoxy-2,2-dichloro-1-(2-methoxyphenyl)ethane (3c): Colorless needles; mp 108—109 °C (from ethanol); IR 1750 cm^{-1} (OAc); ^{1}H NMR (CDCl$_3$) δ=2.16 (3H, s, OAc), 3.78 (3H, s, OCH$_3$), 6.12 (1H, d, J=4.0 Hz, -CHCl$_2$), 6.57 (1H, d, J=4.0 Hz, >CHOAc), and 6.7—7.5 (4H, m, ar.H); MS *m/z* (rel intensity) 262, 264, 266 (M$^+$, 17), 179 (35), 137 (100), and 107 (45). Anal. ($C_{11}H_{12}Cl_2O_3$) C, H.

2*H*-1-Benzopyran-2-one (6): Mp 65—66 °C.

Oxidation Product of (*E*)-3-(4-Chlorophenyl)propenoic Acid (1e). 1,2,2-Trichloro-1-(4-chlorophenyl)ethane (2e): Colorless liquid.[21]

Oxidation Products of (*E*)-3-(4-Methylphenyl)propenoic Acid (1f). 1,2,2-Trichloro-1-(4-methylphenyl)ethane (2f): The ^{1}H NMR data agreed with those reported.[18]

1-Acetoxy-2,2-dichloro-1-(4-methylphenyl)ethane (3f): Colorless liquid.[22] **2,2-Dichloro-1-(4-methylphenyl)ethanol (4f):** Colorless liquid.[23] **4-Methylbenzoic acid:** Mp 180 °C.

Oxidation Products of (*E*)-3-(3-Nitrophenyl)propenoic Acid (1g). 1,2,2-Trichloro-1-(3-nitrophenyl)ethane (2g): Colorless cubes; mp 59.8—60.7 °C (from methanol); IR 1534 and 1354 cm^{-1} (NO$_2$); ^{1}H NMR (CCl$_4$) δ=5.32 (1H, d, J=5.4 Hz, >CHCl), 6.05 (1H, d, J=5.4 Hz, -CHCl$_2$), 7.4—8.0 (2H, m, H-5 and H-6), and 8.1—8.4 (2H, m, H-2 and H-4). Anal. ($C_8H_6Cl_3NO_2$) C, H, N.

β,β-Dichloro-3-nitrostyrene (7): Colorless silky needles; mp 54.9—55.4 °C (from hexane); IR 1610 (C=C), 1531 and 1354 cm^{-1} (NO$_2$); ^{1}H NMR (CCl$_4$) δ=6.90 (1H, s, =CH-), 7.4—8.0 (2H, m, H-5 and H-6), and 8.0—8.5 (2H, m, H-2 and H-4). Anal. ($C_8H_5Cl_2NO_2$) C, H, N.

Oxidation Products of (*E*)-2,3-Diphenylpropenoic Acid (8a). 2,2-Dichloro-1,2-diphenylethanone (9a): Mp 62—63 °C (lit,[24] mp 61—62 °C). **2-Acetoxy-1,2-diphenylethanone (10a):** Mp 81—82 °C (lit,[25] mp 80—82 °C). **1,2-Diphenylethanedione (11a):** Mp 95 °C. **Benzoic acid (12):** Mp 122 °C. **1,2,2-Trichloro-1,2-diphenylethane (13a):** Mp 101—102 °C (lit,[26] mp 102—103 °C). **(*E*)-1,2-Dichloro-1,2-diphenylethene (14):** Mp 140.3—140.5 °C (lit,[27] mp 139 °C).

Oxidation Products of (*E*)-2-(4-Methoxyphenyl)-3-phenylpropenoic Acid (8b). 2,2-Dichloro-1-(4-methoxyphenyl)-2-phenylethanone (9b): Colorless needles; mp 57—58 °C (from ethanol); IR 1689 cm^{-1} (C=O); ^{1}H NMR (CDCl$_3$) δ=3.70 (3H, s, OCH$_3$), 6.71 (2H, m, H-3 and H-5), 7.1—7.8 (5H, m, Ph), and 7.76 (2H, m, H-2 and H-6). Anal. ($C_{15}H_{12}Cl_2O_2$) C, H.

2-Acetoxy-1-(4-methoxyphenyl)-2-phenylethanone (10b):

Mp 79.2—79.9 °C (lit,[28] mp 78—79 °C). **1-(4-Methoxyphenyl)-2-phenylethanedione (11b):** Mp 63 °C (lit,[29] mp 62—63 °C).

Oxidation Products of (*E*)-2,3-Bis(4-methoxyphenyl)propenoic Acid (8c). 2-Acetoxy-1,2-bis(4-methoxyphenyl)ethanone (10c): Mp 93.8—94.8 °C (lit,[30] mp 93.5 °C). **1,2-Bis(4-methoxyphenyl)ethanedione (11c):** Mp 132.7—133.3 °C (lit,[31] mp 133 °C).

Oxidation Products of (*E*)-3-(4-methoxyphenyl)-2-phenylpropenoic Acid (8d). 2-Acetoxy-2-(4-methoxyphenyl)-1-phenylethanone (10d): Colorless liquid.[32] **1-(4-Methoxyphenyl)-2-phenylethanedione (11b).**

Oxidation Products of 3,3-Diphenylpropenoic Acid (15a). 2,2-Dichloro-1,1-diphenylethene (16a): Mp 78.7—79.9 °C (lit,[33] mp 80 °C). **1-Acetoxy-2,2-dichloro-1,1-diphenylethane (17a):** Mp 98.7—99.2 °C (lit,[34] 102.4—104 °C). **2,2-Dichloro-1,1-diphenylethanol (18a):** Mp 95.7—96.7 °C (lit,[35] mp 94—97 °C). **Benzophenone (19a):** Mp 48 °C.

Oxidation Products of 3,3-Bis(4-methoxyphenyl)propenoic Acid (15b). 2,2-Dichloro-1,1-bis(4-methoxyphenyl)ethene (16b): Mp 110.3—110.6 °C (lit,[36] mp 109 °C).

2,2-Dichloro-1,1-bis(4-methoxyphenyl)ethanol (18b): Colorless cubes; mp 103.5—104.5 °C (from ethanol): IR 3568 cm^{-1} (OH): ^{1}H NMR (CDCl$_3$) δ=3.31 (1H, br s, OH), 3.65 (6H, s, 2×OCH$_3$), 6.47 (1H, s, -CHCl$_2$), 6.78 (4H, m, H-3′, H-3″, H-5′, and H-5″), and 7.37 (4H, m, H-2′, H-2″, H-6′, and H-6″). Found: *m*/*z* 326.0453. Calcd for $C_{16}H_{16}{}^{35}Cl_2O_3$: M, 326.0477.

2-Hydroxy-2,2-bis(4-methoxyphenyl)ethanal (20): Colorless liquid: IR 3488 (OH) and 1720 cm^{-1} (CHO); ^{1}H NMR (CDCl$_3$) δ=3.78 (6H, s, 2×OCH$_3$), 4.30 (1H, br s, OH), 6.84 (4H, m, H-3′, H-3″, H-5′, and H-5″), 7.24 (4H, m, H-2′, H-2″, H-6′, and H-6″), and 9.84 (1H, s, CHO). Found: *m*/*z* 272.1040. Calcd for $C_{16}H_{16}O_4$: M, 272.1049.

Oxidation Products of Fluorenylideneacetic Acid (15c). 9-Acetoxy-9-(dichloromethyl)fluorene (17c): Colorless cubes; mp 83.6—84.6 °C (from ethanol); IR 1745 cm^{-1} (OAc); ^{1}H NMR (CCl$_4$) δ=1.94 (3H, s, OAc), 6.79 (1H, s, -CHCl$_2$), and 7.1—7.8 (8H, m, ar.H). Anal. ($C_{16}H_{12}Cl_2O_2$) C, H.

9-Chloro-9-(dichloromethyl)fluorene (21): Colorless cubes; mp 88.0—88.6 °C (from ethanol); ^{1}H NMR (CCl$_4$) δ=6.14 (1H, s, -CHCl$_2$), and 7.0—7.7 (8H, m, ar.H). Anal. ($C_{14}H_9Cl_3$) C, H.

9-Fluorenone (19c): Mp 83 °C.

Oxidation Products of 1-Cyclohexenecarboxylic Acid (22). 2,2,6,6-Tetrachlorocyclohexanone (23): Mp 83.1—83.8 °C (lit,[37] mp 83 °C).

The acidic products of the oxidation of **22** were separated and identified after methylation with diazomethane.

Methyl 1,2-Dichlorocyclohexanecarboxylate (Methyl Ester of 24): Colorless liquid; IR 1740 cm^{-1} (-COO-); ^{1}H NMR (CCl$_4$) δ=1.0—2.7 (8H, m, -CH$_2$-), 3.73 (3H, s, OCH$_3$), and 4.52 (1H, br, -CHCl-); MS (for the acid **24**) *m*/*z* (rel intensity) 197, 199, 201 (100, (M+1)$^+$), 161, 163 (28), 133, 135 (51), and 127 (72).

Methyl 1-Acetoxy-2-chlorocyclohexanecarboxylate (Methyl Ester of 25): Colorless liquid; IR 1735 cm^{-1} (OAc and -COO-); ^{1}H NMR (CCl$_4$) δ=0.7—2.5 (8H, m, -CH$_2$-); 2.04 (3H, s, OAc), 3.70 (3H, s, OCH$_3$), and 4.19 (1H, br, -CHCl-); MS *m*/*z* (rel intensity) 235, 237 (100, (M+1)$^+$). Found: *m*/*z* 235.0729. Calcd for $C_{10}H_{16}{}^{35}ClO_4$: M, 235.0737.

Reaction of 2,3-Dichloro-3-phenylpropanoic Acid (27). A mixture of **27** (203 mg), manganese(III) acetate (497 mg), and lithium chloride (236 mg) in AcOH (25 cm^3) was heated under reflux for 110 min. The reaction mixture was diluted with water and extracted with benzene. After removal of the solvent in vacuo, the resulting substance was separated on TLC with chloroform as the developing solvent to give **2a** (33 mg, 17%) and **27** recovered (120 mg, 59%).

Conversion of 2c to 3c. A mixture of **2c** (86 mg), manganese(II) acetate tetrahydrate (704 mg), and acetic anhydride (1 cm^3) in AcOH (20 cm^3) was heated under reflux for 3 h. The reaction mixture was diluted with water and extracted with benzene. The solvent was evaporated in vacuo and the resulting substance was separated on TLC with benzene as the developing solvent to give **3c** (24 mg, 27%) and **2c** recovered (42 mg, 52%).

Oxidation of 1-Chloro-2-phenylethene (26a). The reaction of 1-chloro-2-phenylethene (**26a**)[38] under the reaction conditions similar to those for **1a** gave 1,2,2-trichloroethane (**2a**) and 1-acetoxy-2,2-dichloro-1-phenylethane (**3a**) (Table 1).

Oxidation of 2-Chloro-1,1-diphenylethene (26b). A similar reaction of 2-chloro-1,1-diphenylethene (**26b**) gave 2,2-dichloro-1,1-diphenylethene (**16a**), 1-acetoxy-2,2-dichloro-1,1-diphenylethane (**17a**), and 2,2-dichloro-1,1-diphenylethanol (**18a**) (Table 3).

Oxidation of 1-Chloro-1,2-diphenylethene (26c). The reaction of 1-chloro-1,2-diphenylethene (**26c**)[27] gave 2,2-dichloro-1,2-diphenylethanone (**9a**), 1,2-diphenylethanedione (**11a**), 1,1,2-trichloro-1,2-diphenylethane (**13a**), and (*E*)-1,2-dichloro-1,2-diphenylethene (**14**) (Table 2).

Conversion of 1,1,2-Trichloro-1,2-diphenylethane (13a) to 2-Chloro-1,2-diphenylethanone (28). A mixture of 1,1,2-trichloro-1,2-diphenylethane (**13a**, 260 mg), manganese(II) acetate tetrahydrate (1.79 g), and acetic anhydride (2.8 cm^3) in AcOH (25 cm^3) was heated under reflux for 3h. After removal of the solvent in vacuo, the resulting substance was separated on TLC with chloroform as the developing solvent to give 2-chloro-1,2-diphenylethanone (**28**) (143 mg) and **13a** (39 mg) (80% conversion).

Oxidation of (*E*)-3-(4-Methoxyphenyl)-2-(4-nitrophenyl)propenoic Acid (8e). (*E*)-3-(4-Methoxyphenyl)-2-(4-nitrophenyl)propenoic acid (**8e**) gave 1,1,2-trichloro-2-(4-methoxyphenyl)-1-(4-nitrophenyl)ethane (**13e**), 2-acetoxy-1,1-dichloro-2-(4-methoxyphenyl)-1-(4-nitrophenyl)ethane (**29e**), 2-acetoxy-2-(4-methoxyphenyl)-1-(4-nitrophenyl)ethanone (**10e**), *p*-anisic acid, and *p*-nitrobenzoic acid.

1,1,2-Trichloro-2-(4-methoxyphenyl)-1-(4-nitrophenyl)ethane (13e): Colorless cubes; mp 127.3—127.8 °C (from ethanol); IR 1599 and 1350 cm^{-1} (NO$_2$); ^{1}H NMR (CDCl$_3$) δ= 3.78 (3H, s, OCH$_3$), 5.47 (1H, s, -CHCl-), 6.74 (2H, m, H-3″ and H-5″), 7.16 (2H, m, H-2″ and H-6″), 7.79 (2H, m, H-2′ and H-6′), and 8.18 (2H, m, H-3′ and H-5′); MS *m*/*z* (rel intensity) 359, 361, 363, 365 (M$^+$, 2), 289, 291 (11), 165 (18), and 154, 156 (100). Anal. ($C_{15}H_{12}Cl_3NO_3$) C, H, N.

2-Acetoxy-1,1-dichloro-2-(4-methoxyphenyl)-1-(4-nitrophenyl)ethane (29e): Colorless plates; mp 136.5—137.5 °C (from methanol); IR 1752 (OAc), 1529 and 1352 cm^{-1} (NO$_2$); ^{1}H NMR (CDCl$_3$) δ=2.10 (3H, s, OAc), 3.74 (3H, s, OCH$_3$), 6.31 (1H, s, CHOAc), 6.68 (2H, m, H-3″ and H-5″), 7.03 (2H, m, H-2″ and H-6″), 7.76 (2H, m, H-2′ and H-6′), and 8.15 (2H, m, H-3′ and H-5′). Anal. ($C_{17}H_{15}Cl_2NO_5$) C, H, N.

2-Acetoxy-2-(4-methoxyphenyl)-1-(4-nitrophenyl)ethanone (10e): Colorless liquid; IR 1740 (OAc), 1704 (C=O), 1530 and 1347 cm^{-1} (NO$_2$); ^{1}H NMR (CDCl$_3$) δ=2.19 (3H, s, OAc), 3.78 (3H, s, OCH_3), 6.79 (1H, s, >CHOAc), 6.90 (2H, m, H-3″ and H-5″), 7.40 (2H, m, H-2″ and H-6″), 8.00 (2H, m, H-2′ and H-6′), and 8.23 (2H, m, H-3′ and H-5′). Found: m/z 329.0860. Calcd for $C_{17}H_{15}NO_6$: M, 329.0899.

p-Anisic Acid: Mp 183.5—184.0 °C. **p-Nitrobenzoic Acid:** Mp 240 °C (subl.).

Conversion of 2,2-Dichloro-1,2-diphenylethanone (9a) to 1,2-Diphenylethanedione (11a). A mixture of **9a** (80 mg), manganese(II) acetate tetrahydrate (450 mg), and acetic anhydride (0.7 cm^3) was heated under reflux for 1h. The reaction mixture was diluted with water and extracted with benzene. The solvent was evaporated in vacuo and the resulting substance was separated on TLC with benzene as the developing solvent to give **11a** (7 mg, 12%) and **9a** recovered (63 mg, 79%).

Conversion of 1,2-Dichlorocyclohexanecarboxylic Acid (24) to 1-Acetoxy-2-chlorocyclohexanecarboxylic Acid (25). A mixture of **24** (71 mg), manganese(II) acetate tetrahydrate (528 mg), and acetic anhydride (0.8 cm^3) in AcOH (20 cm^3) was heated under reflux for 3h. The reaction mixture was diluted with water and then extracted with benzene. After removal of the solvent in vacuo, a mixture of **24** and **25** was obtained in the molar ratio of **24**:**25**=3:2 (identified by ^{1}H NMR spectrum).

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