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Reactions of α,β-Unsaturated Carboxylates, Malonates and Phenylacetates with Manganese(III) Acetate in the Presence of Chloride Ions

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Synopsis. The reaction of alkyl (*E*)-3-phenylpropenoates with manganese(III) acetate in the presence of Cl^- ions gave alkyl (*Z*)-2-chloro-3-phenylpropenoates and alkyl 2,3-dichloro-3-phenylpropanoates. Ethyl (*E*)-2,3-diphenylpropenoate yielded ethyl 2,3-dichloro-2,3-diphenylpropanoate. Alkyl 3,3-diphenylpropenoates gave mainly alkyl 2-chloro-3,3-diphenyl-propenoates. Ethyl 1-cyclohexenecarboxylate gave ethyl 1,2-dichlorocyclohexanecarboxylate. Dimethyl malonate yielded dimethyl dichloromalonate and tetramethyl 1,2-dichloro-1,1,2,2-ethanetetracarboxylate. Substituted malonates resulted in α-chloro derivatives. Methyl phenylacetates gave α-acetoxy derivatives.

Although there have been many investigations into the reaction of manganese(III) acetate,[1] the reaction of this reagent in the presence of the Cl^- ion, which forms a complex, has not been fully examined. In connection with earlier studies of the reactions of aromatic compounds,[2] olefins,[2,3] aryl ketones,[4] and phenyl-substituted propenoic acids,[5] we have now examined the reaction of several kinds of esters with the complex in the hope that this would give chlorinated compounds: we found that α,β-unsaturated esters, malonates, and phenylacetates are reactive towards this complex. We will describe these reactions in this paper.

Results and Discussion

α,β-Unsaturated Esters. The reaction of ethyl (*E*)-3-phenylpropenoate (**1a**) with the manganese(III)-Cl^- complex at a molar ratio of **1a**: Mn(III): Cl^- of 1 : 6 : 12,[6,7] resulted in two products, ethyl 2,3-dichloro-3-phenylpropanoate (**2a**) and ethyl (*Z*)-2-chloro-3-phenylpropenoate (**3a**). The former was the major product. When methyl (*E*)-3-(4-chlorophenyl)propenoate (**1b**) was oxidized with the complex, methyl 2,3-dichloro-3-(4-chlorophenyl)propanoate (**2b**) and methyl (*Z*)-2-chloro-3-(4-chlorophenyl)propenoate (**3b**) were obtained similarly, but in this case **3b** was predominant. Methyl (*E*)-3-(3-nitrophenyl)propenoate (**1c**) and methyl (*E*)-3-(4-methylphenyl)propenoate (**1d**) gave the corresponding 2-chloro derivatives (**3c** and **3d**), while **1d** also yielded **2d** and methyl 3-acetoxy-2-chloro-3-(4-methylphenyl)propanoate (**4d**). When methyl (*E*)-(4-methoxyphenyl)propenoate (**1e**) was oxidized with the complex, methyl (*Z*)-2-chloro-3-(4-methoxyphenyl)propenoate (**3e**), methyl 2-acetoxy-3-chloro-3-(4-methoxyphenyl)propanoate (**4e**) and *p*-anisic acid (**5**) were obtained (Table 1, Entries 1—5).

The reaction of methyl (*E*)-2,3-diphenylpropenoate (**6**) with the manganese(III) acetate-Cl^- complex gave methyl 2,3-dichloro-2,3-diphenylpropanoate (**7**) exclusively (Entry 6).

The reactions of alkyl 3,3-diphenylpropenoates (**8a** and **8b**) gave 2-chloro derivatives (**9a** and **9b**) as the major products, while ethyl 9-fluorenylideneacetate (**8c**) yielded ethyl 9-fluorenylidenechloroacetate (**9c**) and ethyl (9-acetoxy-9-fluorenyl)chloroacetate (**12**) (Entries 7, 8, and 9). The reaction of ethyl 1-cyclohexenecarboxylate (**13**) with the complex yielded only ethyl 1,2-dichloro-1-cyclohexanecarboxylate (**14**) (Entry 10).

Dialkyl Malonates (15a—f). When diethyl methylmalonate (**15a**) was oxidized with the manganese(III) acetate-Cl^- complex, it gave diethyl α-(chloro)-methylmalonate (**16a**) in an excellent yield (Entry 11). Butyl (**15b**) and benzylmalonate (**15c**) yielded monochloro derivatives (**16b** and **16c**) (Entries 12 and 13). Dimethyl chloromalonate (**15d**) gave dimethyl dichloromalonate (**16d**) (Entry 14). Dimethyl malonate (**15e**), on the other hand, yielded two products: dimethyl dichloromalonate (**16d**) and a dimeric compound (**17d**) which was also obtained by the reaction of **15d** with manganese(III) acetate alone (Entries 15 and 16). Dimethyl bromomalonate (**15f**) gave a mixture of various products, from which only tetramethyl 1,2-dibromo-1,1,2,2-ethanetetracarboxylate (**17f**) was isolated and that is in a poor yield (Entry 17). The **15f** yielded tetramethyl ethenetetracarboxylate (**18**) on prolonged heating when the reaction was conducted with manganese(III) acetate alone (Entry 19).

Methyl Phenylacetates (19a and 19b). The reactions of methyl 4-methoxyphenylacetate (**19a**) and methyl 3,4-dimethoxyphenylacetate (**19b**) yielded α-acetoxy derivatives (**20a** and **20b**) in good yields (Entries 20 and 22). When **19a** was oxidized with manganese(III) acetate alone over a prolonged reaction time, methyl 3-(acetoxymethyl)-4-methoxyphenylacetate (**21**) was obtained in a minor quantity, together with **20a** (Entry 21). Unsubstituted ethyl phenylacetate was found to be unreactive towards the manganese(III) acetate-Cl^- complex under the present reaction conditions.

Conclusion. The reaction of methyl (*E*)-3-phenylpropenoate with the manganese(III) acetate-Cl^- was previously briefly reported to give methyl 2,3-dichloro-3-phenylpropanoate and methyl (*E*)-2-chloro-3-phenylpropenoate.[3] However, we found that a substituent on the aromatic ring and an extra phenyl group at the C-2 or C-3 change the product distribution completely. The reaction of methyl (*E*)-3-(4-chlorophenyl)propenoate (**1b**) gave the 2-chloro derivative (**3b**) as the major product, while methyl (*E*)-3-(4-methoxyphenyl)propenoate (**1e**) yielded methyl 3-acetoxy-2-chloro-3-(4-methoxyphenyl)propanoate (**4e**). The reaction of **1e** ended in a shorter reaction time compared with the others, whereas **1c**, which has an electron-withdrawing nitro group, was less reactive and 25% of the **1c** was

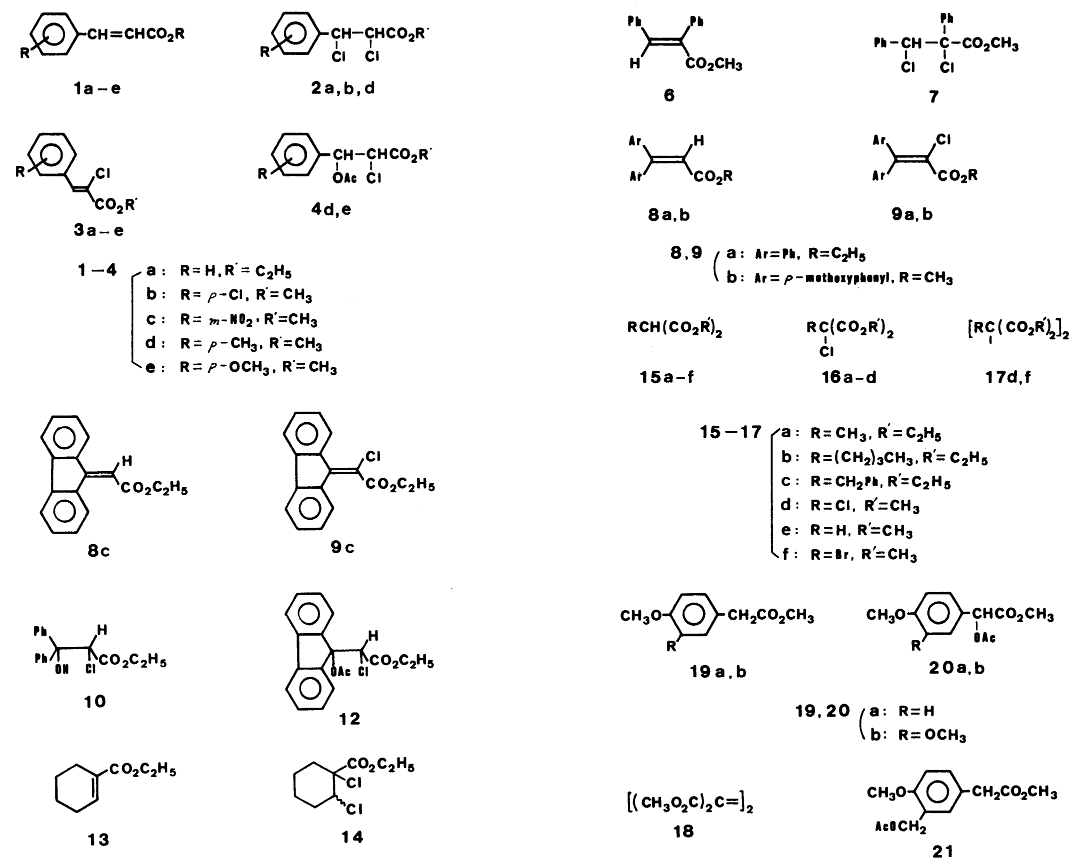

Fig. 1.

Table 1. Reaction of Esters with Manganese(III) Acetate in the Presence of LiCl$^{a)}$

Entry	Substrate	Molar ratio$^{b)}$	Reaction time/min	Product yield$^{c)}$/%
1	**1a**	1 : 6 : 12	310	**2a**$^{8)}$(59), **3a**$^{9)}$(14)
2	**1b**	1 : 8 : 16	440	**2b**$^{10)}$(33), **3b**$^{11)}$(49)
3	**1c**	1 : 10 : 15	450	**3c**$^{11)}$(35)$^{d)}$
4	**1d**	1 : 8 : 16	410	**2d**$^{10)}$(13), **3d**$^{12)}$(34), **4d**$^{11)}$(21)
5	**1e**	1 : 6 : 12	180	**3e**(17), **4e**$^{13)}$(59), **5**(21)
6	**6**	1 : 8 : 24	340	**7**(84)
7	**8a**	1 : 6 : 12	460	**9a**$^{14)}$(66), **10**(13)
8	**8b**	1 : 3 : 10	30	**9b**(74), **11**$^{15)}$(19)
9	**8c**	1 : 6 : 18	250	**9c**(24), **12**(65)
10	**13**	1 : 6 : 18	310	**14**(83)
11	**15a**	1 : 3 : 10	80	**16a**$^{16)}$(88)
12	**15b**	1 : 3 : 10	41	**16b**$^{17)}$(90)
13	**15c**	1 : 3 : 10	60	**16c**$^{18)}$(95)
14	**15d**	1 : 3 : 10	94	**16d**$^{19)}$(69)
15	**15d**	1 : 1.2 : 0	65	**17d**(60)
16	**15e**	1 : 3.4 : 10	16	**16d**(55), **17d**(18)
17	**15f**	1 : 3 : 10	110	**17f**(17)
18	**15f**	1 : 1.2 : 0	60	**17f**(31)
19	**15f**	1 : 3 : 0	215	**18**$^{20)}$(76)
20	**19a**	1 : 2.5 : 10	30	**20a**(94)
21	**19a**	1 : 3 : 0	540	**20a**(41), **21**(16)$^{e)}$
22	**19b**	1 : 2.5 : 10	6	**20b**(84)

a) The reaction was carried out at the reflux temperature. b) Substrate: Mn(III): LiCl. c) Isolated yields based on the substrate added. All products were reasonably pure after TLC separation. d) **1c** (25%) was recovered. e) **19a** (39%) was recovered.

recovered even when an excess of the reagent was used. A phenyl group at the C-2 in a propenoate favors the formation of 1,2-dichloro compound **7**, while a phenyl group at the C-3 makes 2-chloro derivatives (**9a** and **9b**) the major products. The reactions of malonic esters and methoxy-substituted phenylacetates with the manganese(III) acetate-Cl$^-$ complex gave α-chloro and α-acetoxy derivatives respectively in excellent yields. These can be useful in organic synthesis.

Table 2. Physical and Spectral Data for the Reaction Products[a)]

Compound	Mp (θ_m/°C) (solvent)[b)]	ν/cm^{-1}[c)]	δ/ppm[d)]
3e	58.8—59.8 (Diethyl ether–Light petroleum)	1717	3.78 (3H, s), 3.82 (3H, s), 6.86 (2H, m), 7.77 (2H, m), 7.79 (1H, s)
7[e)]	Liquid	1735	3.57 (3H, s), 5.79 (1H, s), 6.9—7.5 (10H, m) 3.68 (3H, s), 5.74 (1H, s), 6.9—7.5 (10H, m)
9b	92.8—93.8 (Ethanol)	1719	3.57 (3H, s), 3.75 (6H, s), 6.7—7.3 (8H, m)
9c	72.4—72.6 (Ethanol)	1727	1.39 (3H, t, J=7.2 Hz), 4.42 (2H, q, J=7.2 Hz), 7.1—7.6 (7H, m), 8.2—8.4 (1H, m)
10	122—122.6 (Ethanol)	1725 3500	1.00 (3H, t, J=6.6 Hz), 4.01 (2H, q, J=6.6 Hz), 4.55 (1H, s), 5.17 (1H, s), 7.1—7.6 (10H, m)
12	Liquid	1747	0.72 (3H, t, J=7.2 Hz), 1.90 (3H, s), 3.70 (2H, q, J=7.2 Hz), 5.36 (1H, s), 7.1—7.8 (8H, m)
14	Liquid	1740	1.32 (3H, t, J=7.2 Hz), 1.2—2.7 (8H, m), 4.20 (2H, q, J=7.2 Hz), 4.56 (1H, m)
17d	91—92 (Methanol–Light petroleum)	1745 1760	3.80 (s)
17f	103.5 (Methanol)	1732 1750	3.84 (s)
20a	Liquid	1742	2.09 (3H, s), 3.64 (3H, s), 3.75 (3H, s), 5.79 (1H, s), 6.78 (2H, m), 7.29 (2H, m)
20b	Liquid	1746 1755	2.06 (3H, s), 3.60 (3H, s), 3.72 (3H, s), 3.74 (3H, s), 5.65 (1H, s), 6.6—7.1 (3H, m)
21	Liquid	1732	1.99 (3H, s), 3.41 (2H, s), 3.56 (3H, s), 3.74 (3H, s), 5.00 (2H, s), 6.74 (1H, m), 7.0—7.2 (2H, m)

a) Either the elemental analyses or the high-resolution mass spectra for the new compounds agreed with the calculated values. b) For recrystallization. c) In $CHCl_3$. d) The ^1H NMR spectra were determined in $CDCl_3$ for compounds **3e**, **7**, **9b**, **10**, and in CCl_4 for others. e) A mixture of two diastereoisomers.

Experimental

Oxidation of Propenoates (1a—e, 6 and 8a—c), Malonates (15a—f), and Phenylacetates (19a and 19b) with the Manganese(III) Acetate-Chloride Ions. The general procedure for the oxidation of esters was as follows. A mixture of an ester (1 mmol), manganese(III) acetate,[6)] and chloride ions in the molar ratio shown in Table 1 in acetic acid (30 cm^3) was heated under reflux until the color of the solution had changed from brown to transparent. After the 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 evaporated in vacuo, and the products were separated on preparative TLC (Kieselgel 60G or Wakogel B-10), with chloroform or benzene as the developing solvent. The yields are summarized in Table 1. The known compounds were identified by comparing them with the spectral data and/or the melting points in the literature. The physical and spectral data for the new compounds are summarized in Table 2.

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