The Reaction of Acetophenones with Manganese(III) Acetate

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The reaction of 4′-methoxyacetophenone with manganese(III) acetate in the presence of ammonium chloride yielded 2-chloro-4′-methoxyacetophenone (**2a**) and 2,2-dichloro-4′-methoxyacetophenone (**3a**). The reaction of **2a** with these reagents gave **3a**, 4′-methoxy-2,2,2-trichloroacetophenone, and 1,4-bis(4-methoxyphenyl)-2,2,3,3-tetrachloro-1,4-butanedione (**8a**). The reactions of **2a** and 2-bromoacetophenone with manganese(III) acetate yielded the corresponding 2,3-dihalo-1,4-diphenyl-1,4-butanediones, 1,4-diphenyl-2-halo-2-butene-1,4-diones, 2,3-dihalo-2-butene-1,4-diones, 2,2-dibromoacetophenone, and **8a**. The reaction pathways are discussed.

It has been reported that the reaction of acetophenone with oxygen in the presence of manganese(III) acetate in butyric acid gave benzoic acid.[1] The reactions of aliphatic and cyclic ketones with manganese(III) acetate have also been reported to give α-acetoxy ketones as the major product when the reaction was conducted under nitrogen.[2] The reactions of ketones with manganese(III) acetate in the presence of olefins have been reported by many investigators.[2—6] It seems that the chloride ion, in place of olefins, oxygen and acetate ion, will react with the benzoylmethyl radical formed from acetophenone. The acetophenone derivatives examined are 4′-methoxyacetophenone (**1a**) and 2-chloro-4′-methoxyacetophenone (**2a**). The reactions were carried out in boiling acetic acid. The structure of the reaction products were determined by means of the study of their IR, NMR, and mass spectra, by elemental analyses, and by comparison with authentic samples.

When **1a** was oxidized with manganese(III) acetate–ammonium chloride in acetic acid containing acetic anhydride, 2-chloro-4′-methoxyacetophenone (**2a**) and 2,2-dichloro-4′-methoxyacetophenone (**3a**) were obtained (Table 1, Entries 2—9), in contrast to the reaction in the absence of ammonium chloride (Entry 1), which gave 2-acetoxy-4′-methoxyacetophenone (**2b**) and *p*-anisic acid (**4a**). The yields of **2a** were first increased and then decreased with the increase in the oxidant, while the yields of **3a** were increased (Entries 2, 4, and 8). The total yields decreased with a higher molar ratio of the oxidant to the substrate, because of the formation of a number of undefined products. It was also found that acetic anhydride added to the reaction mixture effected the yield of **3a** more than that of **2a** (Entries 3, 4, 5, and 6), although no rational explanation could be given. Lithium chloride and hydrochloric acid were also employed as chloride-ion sources; the results are shown in the table (Entries 10 and 11). It could be assumed that the reaction is initiated by the formation of the benzoylmethyl radical[1] (Ia in Scheme 1), which captures the chloride ion in the presence of manganese(III) acetate, but this is the least possible because it is difficult for the three species to get together at one time. It seems reasonable to

$$\mathrm{ArCOCH_2^{\cdot} + Cl^- + Mn(III) \longrightarrow ArCOCH_2Cl + Mn(II)}$$

assume that the chloride ion either forms a complex

TABLE 1. THE REACTIONS OF 4′-METHOXYACETOPHENONE (**1a**) AND 2-CHLORO-4′-METHOXYACETOPHENONE (**2a**) WITH MANGANESE (III) ACETATE IN THE PRESENCE OF AMMONIUM CHLORIDE IN ACETIC ACID CONTAINING ACETIC ANHYDRIDE AT THE REFLUX TEMPERATURE

Entry	Substrate	Reaction conditions: Molar ratio of substrate: oxidant : Ac_2O	Reaction conditions: Time / min	Products (yield/%)[a)]: 2a	2b	3a	4a	5a	8a	Recovered substrate / %
1	**1a**	1 : 2 : 0[b)]	60		24		22			40
2	**1a**	1 : 2 : 8	12	33		7				49
3	**1a**	1 : 3 : 6	17	34		26				39
4	**1a**	1 : 3 : 12	15	38		21				28
5	**1a**	1 : 3 : 24	10	40		14				30
6	**1a**	1 : 3 : 48	7	25		2				52
7	**1a**	1 : 4 : 8	22	16		29				25
8	**1a**	1 : 4 : 16	20	22		45				14
9	**1a**	1 : 4 : 32	15	16		28				40
10	**1a**	1 : 3 : 12[c)]	12	16		22				20
11	**1a**	1 : 3 : 40[d)]	10	15		18				25
12	**2a**[a)]	1 : 2 : 4	11	—		47				57
13	**2a**	1 : 3 : 6	21	—		41		10	4	13

a) The yields are based on the amount of the substrate used. b) The reaction was carried out in the absence of ammonium chloride. c) Lithium chloride (20 mmol) was used in place of ammonium chloride. d) 12 M Hydrochloric acid (9 mmol) was used in place of ammonium chloride.

TABLE 2. THE REACTIONS OF 2-HALOACETOPHENONES (**2a** AND **2c**) AND 2,2-DIHALOACETOPHENONES (**3a** AND **3c**) WITH MANGANESE(III) ACETATE IN ACETIC ACID AT THE REFLUX TEMPERATURE

Entry	Substrate	Reaction conditions: Molar ratio of substrate: oxidant : Ac_2O	Time/min	Products (yield/%) 3	4	8	9	10	11	Recovered substrate/%
1	**2a**	1 : 2 : 0	95	0	10	8	9	40	5	0
2	**2c**	1 : 1 : 0	14	9	0	0	12	8	0	31
3	**2c**	1 : 2 : 0	45	8	0	0	8	23	8	0
4	**2c**	1 : 2 : 8	25	4	0	0	6	20	3	2
5	**2c**+**3c**[b)]	1 : 2 : 0	60	—	0	0	1	12	21	5,[c)] 12[d)]
6	**3a**[9)]	1 : 1 : 0	65	—	0	37	0	0	0	25

a) The yields are based on the amount of the substrate used. b) A mixture of 1 mmol each. c) The recovery of **2c**. d) The recovery of **3c**.

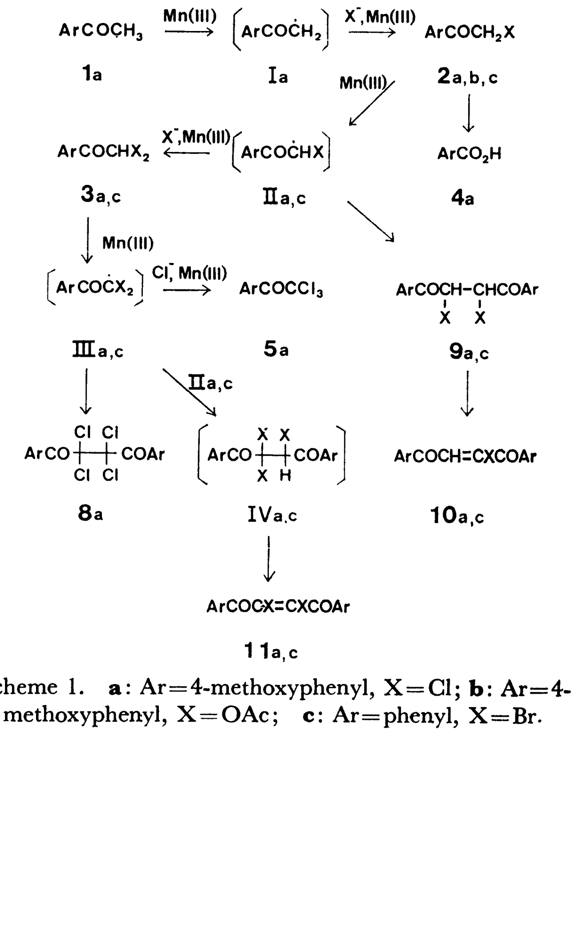
with manganese(III) acetate such as $[Mn(OAc)_3Cl]^-$ or replaces some of the acetate ions to form $Mn(OAc)_{3-n}Cl_n$, which then reacts with Ia. In fact, the visible spectrum of manganese(III) acetate in acetic acid showed a maximum at 470 nm (ε 288) which was shifted to 530 nm (shoulder, ε 439) by the addition of lithium chloride. It has been reported that a similar shift was caused by the addition of potassium acetate.[7)] **2a** can be further chlorinated in the same way to **3a** and **5a** (Table 1, Entries 12 and 13, and Scheme 1).

The reaction of **1a** with chlorine in acetic acid gave 3′-chloro-4′-methoxyacetophenone (**6**) and 2,3′-dichloro-4′-methoxyacetophenone (**7**), along with **2a**. The absence of the nuclear chlorinated compounds among the manganese(III) acetate–ammonium chloride oxidation products from **1a** eliminated the pathway in which the chloride ion is oxidized to chlorine, with the latter then reacting with **1a** to give **2a** and **3a**. Other nucleophiles, such as methanol and benzoic acid, failed to react with **1a**, and **2b** was obtained in poor yields (10 and 6% respectively). When ammonium bromide was used, bromine was liberated.

When 2-chloro-4′-methoxyacetophenone (**2a**) was treated with manganese(III) acetate–ammonium chloride, 1,4-bis(4-methoxyphenyl)-2,2,3,3-tetrachlorobutanedione (**8a**) was obtained, together with **3a** and 4′-methoxy-2,2,2-trichloroacetophenone (**5a**) (Entry 13). **8a** can be formed by the dimerization of the benzoyldichloromethyl radical (IIIa), which is derived from **3a** by the action of manganese(III) acetate. This led us to examine the reactions of **2a** and 2-bromoacetophenone (**2c**) with manganese(III) acetate.

When 2-bromoacetophenone (**2c**) was oxidized with manganese(III) acetate, 2,2-dibromoacetophenone (**3c**), 2,3-dibromo-1,4-diphenyl-1,4-butanedione (**9c**), 2-bromo-1,4-diphenyl-2-butene-1,4-dione (**10c**), and (*E*)-2,3-dibromo-1,4-diphenyl-2-butene-1,4-dione (**11c**) were obtained (Table 2). The yields of the reaction products depended on the molar ratio of the oxidant to the substrate (Entries 2 and 3) and were decreased by the presence of acetic anhydride, which shortened the reaction time considerably (Entry 4). In boiling acetic acid, **9c** was converted to **10c** with the loss of hydrogen bromide. The configurations of **9c** and **10c** could not be determined. When 1 : 1 mixture of **2c** and **3c** was oxidized with manganese(III) acetate, **11c** was obtained in an increased yield, at the expense of decreased yields of **9c** and **10c** (Entry 5). The reaction pathway may be explained as follows. The reaction of **2c** with manganese(III) acetate gives the benzoylbromomethyl radical (IIc), which dimerizes to **9c**. The dehydrobromination of **9c** yields **10c**. IIc, on the other hand, reacts with the hydrogen bromide now present in the reaction mixture to give **3c**. The benzoyldibromomethyl radical (IIIc), which is formed from **3c** by manganese(III) acetate, reacts with IIc to give IVc. The dehydrobromination of IVc gives **11c**. The reaction of 2-chloro-4′-methoxyacetophenone (**2a**) with manganese(III) acetate in acetic acid gave similar products except for the presence of **8a** and the absence of **3a** among the reaction products. The difference in the product distributions in Entry 11 of Table 1 and in Entry of Table 2 may be ascribed to the difference in the chloride-ion concentration. **3a** was converted to **8a** with manganese(III) acetate (Entry 6). These values are shown in Scheme 1.

It is thus concluded that the benzoylmethyl radical



Scheme 1. **a**: Ar=4-methoxyphenyl, X=Cl; **b**: Ar=4-methoxyphenyl, X=OAc; **c**: Ar=phenyl, X=Br.

(Ia) and the benzoylhalomethyl radicals (IIa and IIc) derived from the corresponding acetophenone with manganese(III) acetate can react with the halide ion in the presence of manganese(III) acetate to give **2a**, **3a**, **3c**, and **5a**, and that the benzoylhalomethyl radicals (IIa, IIc, IIIa, and IIIc) tend to dimerize to form **8a**, **9a**, **9c**, **10a**, **10c**, **11a**, and **11c** in low halide-ion concentrations.

Experimental

All the ^{1}H NMR spectra were recorded with a Hitachi-Perkin-Elmer R 24 spectrometer, with tetramethylsilane as the internal reference. The IR spectra were taken for the chloroform solution on a JASCO grating spectrometer, while the UV spectra were recorded for the methanol solution with a Hitachi EPS-3T spectrophotometer. The mass spectra were recorded with a JMS-01 SG-2 instrument. The melting points were determined with a Yanagimoto micro-melting point apparatus and were not corrected.

Acetophenones. The 4′-methoxyacetophenone (**1a**) and 2-bromoacetophenone (**2c**) were commercial samples from Wako Pure Chemical Industries, Ltd. The 2-chloro-4′-methoxyacetophenone (**2a**)[8] and 2,2-dichloro-4′-methoxyacetophenone (**3a**)[9] were prepared by the standard procedure.

Oxidations of 4′-Methoxyacetophenone (1a) and 2-Chloro-4′-methoxyacetophenone (2a) with Manganese(III) Acetate–Ammonium Chloride. The general procedure for the oxidations of **1a** and **2a** with manganese(III) acetate–ammonium chloride was as follows. A mixture of **1a** (or **2a**) (2 mmol), manganese(III) acetate dihydrate,[10] acetic acid (20 ml), acetic anhyride and ammonium chloride (19 mmol) was heated under reflux for the time shown in Table 1. After the removal of the solvent *in vacuo*, 2 M hydroric acid (40 ml) was added to the reaction mixture and the mixture was extract with benzene (30 ml). The benzene solution was washed with aqueous sodium hydrogencarbonate and then evaporated *in vacuo*. The resulting liquid was chromatographed on TLC (Wakogel B10), with benzene or chloroform as the developing solvent. The yields are summarized in Table 1.

2-Chloro-4′-methoxyacetophenone (2a): Mp 100—102 °C (CCl_4) (lit,[8] mp 101—102 °C); IR 1700 and 1710 cm^{-1}; NMR ($CDCl_3$) δ=3.83 (3H, s, OCH_3), 4.58 (2H, s, $-CH_2-$), 6.95 (2H, m, $H_{(3')}$ and $H_{(5')}$), and 7.91 (2H, m, $H_{(2')}$ and $H_{(6')}$).

2,2-Dichloro-4′-methoxyacetophenone (3a): Mp 78—79 °C (CCl_4) (lit,[9] mp 74—75 °C); IR 1700 and 1718 cm^{-1}; NMR (CCl_4) δ=3.82 (3H, s, OCH_3), 6.43 (1H, s, >CH–), 6.79 (2H, m, $H_{(3')}$ and $H_{(5')}$), and 7.90 (2H, m, $H_{(2')}$ and $H_{(6')}$).

4′-Methoxy-2,2,2-trichloroacetophenone (5a): Liquid (lit,[11] mp 33—34.5 °C); IR 1720 cm^{-1}; NMR (CCl_4) δ=3.86 (3H, s, OCH_3), 6.87 (2H, m, $H_{(3')}$ and $H_{(5')}$), and 8.20 (2H, m, $H_{(2')}$ and $H_{(6')}$).

1,4-Bis(4-methoxyphenyl)-2,2,3,3-tetrachloro-1,4-butanedione (8a): Mp 145—146 °C (CCl_4); IR 1708 cm^{-1}; UV λ_{max} 229 (12000) and 304 nm (25900); NMR ($CDCl_3$) δ=3.84 (6H, s, 2×OCH_3), 6.89 (4H, m, $H_{(3')}$, $H_{(3'')}$, $H_{(5')}$, and $H_{(5'')}$), and 8.25 (4H, m, $H_{(2')}$, $H_{(2'')}$, $H_{(6')}$, and $H_{(6'')}$). Found: C, 49.33; H, 3.34%. Calcd for $C_{18}H_{14}Cl_4O_4$: C, 49.57; H, 3.24%.

Chlorination of 4′-Methoxyacetophenone (1a) with Chlorine in Acetic Acid. Through a solution of **1a** (1 g) in acetic acid (10 ml), chlorine gas was passed (The weight of the chlorine absorbed was 0.5 g), after which the solution was left at room temperature for 30 min. After the removal of the acetic acid *in vacuo*, the resulting mixture was chromatographed on TLC, with benzene as the developing solvent, giving unchanged **1a** (74 mg, 7%), 3′-chloro-4′-methoxyacetophenone (**6**) [237 mg, 19%, mp 73—74 °C (MeOH) (lit,[12] mp 71—73 °C)], **2a** (358 mg, 29%), and 2,3′-dichloro-4′-methoxyacetophenone (**7**) [207 mg, 14%, mp 89—90 °C (EtOH); IR 1700 cm^{-1}; NMR ($CDCl_3$) δ=3.96 (3H, s, OCH_3), 4.62 (2H, s, $-CH_2-$), 7.00 (1H, d, J=8.0 Hz, $H_{(5')}$), 7.75—8.05 (2H, m, $H_{(2')}$ and $H_{(6')}$). Found: C, 49.43; H, 3.79%. Calcd for $C_9H_8Cl_2O_2$: C, 49.34; H, 3.68%].

Oxidation of Acetophenones (1a, 2a, 2c, 3a, and 3c) with Manganese(III) Acetate. The general procedure for the oxidation of acetophenones was as follows. A mixture of an acetophenone (2 mmol), manganese(III) acetate dihydrate, and acetic acid (40 ml) was heated under reflux until the color of the manganese(III) ion disappeared. The reaction mixture was then worked-up in a manner similar to the above. The yields are summarized in Table 2.

Oxidation Products of 1a. *2-Acetoxy-4′-methoxyacetophenone (2b)*: Liquid (lit,[13] mp 58—59 °C; IR 1718 (C=O) and 1760 cm^{-1} (OAc); NMR (CCl_4) δ=2.08 (3H, s, OAc), 3.73 (3H, s, OCH_3), 5.07 (2H, s, $-CH_2-$), 6.78 (2H, m, $H_{(3')}$ and $H_{(5')}$), and 7.73 (2H, m, $H_{(2')}$ and $H_{(6')}$).

p-Anisic Acid (4a): Mp 185 °C.

Oxidation Products of 2a. *1,4-Bis(4-methoxyphenyl)-2,3-dichloro-1,4-butanedione (9a)*: Mp 190—191 °C (dec) (CCl_4); IR 1696 cm^{-1} (C=O); UV λ_{max} (ε) 229 (16600) and 300 nm (35000); NMR ($CDCl_3$) δ=3.85 (6H, s, 2×OCH_3), 5.68 (2H, s, >CH–), 6.93 (4H, m, $H_{(3')}$, $H_{(3'')}$, $H_{(5')}$, and $H_{(5'')}$), and 8.00 (4H, m, $H_{(2')}$, $H_{(2'')}$, $H_{(6')}$, and $H_{(6'')}$). Found: C, 58.56; H, 4.45%. Calcd for $C_{18}H_{16}Cl_2O_4$: C, 58.87; H, 4.39%.

1,4-Bis(4-methoxyphenyl)-2-chloro-2-butene-1,4-dione (10a): Liquid; IR 1680 cm^{-1} (C=O); UV λ_{max} (ε) 227 (14600) and 305 nm (19900); NMR (CCl_4) δ=3.68 (s, OCH_3), 3.72 (s, OCH_3), 6.65—6.95 (m, $H_{(3')}$, $H_{(3'')}$, $H_{(5')}$, and $H_{(5'')}$), 7.12 (s, =CH–), 7.30 (s, =CH–), and 7.6—7.9 (m, $H_{(2')}$, $H_{(2'')}$, $H_{(6')}$, and $H_{(6'')}$). The presence of two singlets with nearly equal intensities at δ=7.12 and 7.30 indicated that this substance was a mixture of (Z)- and (E)-isomers in a 1 : 1 molar ratio. MS m/e 330 (M^+), 295 (M^+ $-$Cl), 223 (M^+ $-C_6H_4OCH_3$), 207, 195 (M^+ $-COC_6H_4OCH_3$), 135 ($CH_3OC_6H_4CO^+$), 107, and 92.

1,4-Bis(4-methoxyphenyl)-2,3-dichloro-2-butene-1,4-dione (11a): Mp 132.5—134 °C (CCl_4); IR 1680 cm^{-1} (C=O); UV λ_{max} (ε) 228_{sh} (15200) and 309 nm (25800); NMR (CCl_4) δ=3.78 (6H, s, 2×OCH_3), 6.80 (4H, $H_{(3')}$, $H_{(3'')}$, $H_{(5')}$, and $H_{(5'')}$), and 7.68 (4H, m, $H_{(2')}$, $H_{(2'')}$, $H_{(6')}$ and $O_{(6')}$: Found: C, 59.02; H, 3.62%. Calcd for $C_{18}H_{14}Cl_2O_4$: C, 59.20; H, 3.86%.

1, 4-Bis(4-methoxyphenyl)-2, 2, 3, 3-tetrachloro-1, 4-butanedione (8a): Mp 145—146 °C.

Oxidation Products of 2c. *2,2-Dibromoacetophenone (3c)*: Liquid (lit,[14] mp 36—37 °C); IR 1695 and 1718 cm^{-1}; NMR (CCl_4) δ=6.55 (1H. s. >CH–), 7.2—7.7 (3H, m, $H_{(3')}$, $H_{(4')}$, and $H_{(5')}$), and 7.9—8.2 (2H, m, $H_{(2')}$ and $H_{(6')}$).

2,3-Dibromo-1,4-diphenyl-1,4-butanedione (9c): Mp 180—182 °C (dec) (CCl_4); IR 1710 cm^{-1} (C=O); UV λ_{max} (ε) 264 nm (24200); NMR ($CDCl_3$) δ=5.99 (2H, s, >CH–), 7.2—7.8 (6H, m, $H_{(3')}$, $H_{(3'')}$, $H_{(4')}$, $H_{(4'')}$, $H_{(5')}$, and $H_{(5'')}$), and 8.0—8.25 (4H, m, $H_{(2')}$, $H_{(2'')}$, $H_{(6')}$, and $H_{(6'')}$). Found: C, 48.20; H, 3.07%. Calcd for $C_{16}H_{12}Br_2O_2$: C, 48.52; H, 3.05%.

2-Bromo-1,4-diphenyl-2-butene-1,4-dione (10c): Liquid; IR 1690 cm^{-1} (C=O); UV λ_{max} (ε) 270 nm (20200); NMR (CCl_4) δ=7.2–7.7 (6H, m, $H_{(3')}$, $H_{(3'')}$, $H_{(4')}$ $H_{(4'')}$, $H_{(5')}$, and $H_{(5'')}$), 7.60 (1H, s, =CH–), and 7.7—8.0 (4H, m, $H_{(2')}$. $H_{(2'')}$, $H_{(6')}$, and $H_{(6'')}$); MS m/e 314 (M^+), 235 (M^+ $-$Br), 105 ($PhCO^+$), and 77 (Ph^+). **10c** could be a mixture of (Z)- and (E)-isomers.

(E)-2,3-Dibromo-1,4-diphenyl-2-butene-1,4-dione (11c): Mp 208—210 °C (CCl_4–light petroleum) (lit,[15,16] mp 213 °C);

IR 1685 cm^{-1} (C=O); UV λ_{max} (ε) 266 (16600) and 293 nm (shoulder) (6220); NMR (CCl_4) δ=7.2−7.7 (6H, m, $H_{(3')}$, $H_{(3'')}$, $H_{(4')}$, $H_{(4'')}$, $H_{(5')}$, and $H_{(5'')}$), and 7.7—7.95 (4H, m, $H_{(2')}$, $H_{(2'')}$, $H_{(6')}$, and $H_{(6'')}$). Found: C, 49.07; H, 2.66%. Calcd for $C_{16}H_{10}Br_2O_2$: C, 48.77; H, 2.56%. MS *m/e* 392 (M^+), 313 (M^+ −Br), 129 (PhCOC≡C^+), 105 ($PhCO^+$), and 77 (Ph^+).

Oxidation Products of a Mixture of **2c** *and* **3c**.

2,3-Dibromo-1,4-diphenyl-1,4-butanedione (9c): Mp 180—182 °C (dec).

2-Bromo-1,4-diphenyl-2-butene-1,4-dione (10c): Liquid.

(E)-2,3-Dibromo-1,4-diphenyl-2-butene-1,4-dione (11c): Mp 208—210 °C.

Oxidation Products of **3a**. *1,4-Bis(4-methoxyphenyl)-2,2,3,3-tetrachloro-1,4-butanedione (8a)*: Mp 145—146 °C.

Dehydrobromination of **9c**. A solution of **9c** (40 mg) in acetic acid (1 ml) was heated under reflux for 35 min. The reaction mixture was then worked-up as has been described previously, giving **10c** (18.5 mg, 45%) identical with the sample obtained by the reaction of **2c** with manganese(III) acetate dihydrate, and also unchanged **9c** (12 mg, 30%).

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