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Manganese(III)-Mediated Formylation of Aromatic Compounds in the Presence of Malonic Acid

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The reaction of naphthalenes with malonic acid in the presence of manganese(III) acetate gives naphthalenecarbaldehydes and naphthalenecarboxylic acids. Similar reactions of anthracene, pyrene, and methoxybenzenes also yield formylated and carboxylated products. It was found that the formyl group introduced to the aromatic ring was not derived from carboxymethyl radical generated directly by the thermolysis of manganese(III) acetate, but from a dicarboxymethyl radical formed by the interaction of malonic acid and manganese(III) acetate. In addition, it was also found that the dicarboxymethyl radicals attacked the position of the highest electron density on the aromatic ring and that this formylation was effective when the ionization potential of the aromatic compound was lower than 7.8 eV.

It is known that the reaction of aromatic compounds with manganese(III) acetate, $[Mn_3O(OAc)_6(OAc)(HOAc)]\cdot 5H_2O$ (which is usually abbreviated to $[Mn_3O]$),[1] gives mainly acetoxymethylated products together with small amounts of carboxymethyl, diacetoxymethyl or formyl, and carboxyl derivatives.[2] This reaction is caused by carboxymethyl radicals, $\cdot CH_2CO_2H$, which are formed by the pyrolysis of manganese(III) acetate.[3] Kurosawa and McOmie have obtained a propellane, 7-oxa-10,11-benzotricyclo[4.3.2.0]undeca-2,4,10-trien-8-one, by the use of a similar oxidation of biphenylene.[4] On the other hand, Kurz and Chen have reported on the nitromethylation of aromatic hydrocarbons promoted by manganese(III) acetate.[5] A key of this nitromethylation is the formation of nitromethyl radicals, $\cdot CH_2NO_2$, formed by the

Table 1. Oxidation of Aromatic Compounds with Manganese(III) Acetate in the Presence of Malonic Acid in Boiling Acetic Acid

Entry	Compound	Molar ratio[a]	Time	Product (yield/%)[b]		
			min	Aldehyde	Acid	Others
1	**1a**	1:4:4	1	**2a** (55)		
2	**1a**	1:4:8	1	**2a** (50)		
3	**1a**	1:4:12	2	**2a** (39)		
4[c]	**1a**	1:8:8	10	**2a** (30)		
5[d]	**1a**	1:8:8	3	**2a** (34)		
6	**1a**	1:8:8	1	**2a** (59)		
7	**1a**	1:12:8	1	**2a** (46)		
8	**1b**	1:4:4	1	**2b** (44)		
9	**1b**	1:8:8	1	**2b** (46)	**3b** (12)	
10	**1c**	1:4:4	1	**2c** (33)		
11	**1c**	1:8:8	1	**2c** (25)	**3c** (8)	
12	**1d**	1:8:8	1	**2d** (58)		
13	**1e**	1:8:8	1	**2e** (53)		
14	**1f**	1:8:8	1	**2f** (34)		
15	**1g**	1:8:8	1	**2g** (26)		
				2g′ (22)		
				4 (13)		
16	**1h**	1:8:8	1	**2h** (13)	**3h** (39)	
17	**1i**	1:8:8	1	**2i** (6)	**3i** (22)	
18	**1j**	1:8:8	1	**2j** (5)	**3j** (26)	
19	**1k**	1:8:8	1		**3k** (43)	**5** (9)
20	**1l**	1:8:8	1		**3l** (29)	
21	**6**	1:4:4	1	**8** (12)	**10** (15)	**7** (28) **9** (13)
22	**6**	1:8:8	1	**8** (12)		**7** (16) **9** (10)
23	**11**	1:8:8	1	**12** (25)	**14** (10)	**13** (22)
24	**15a**	1:8:8	1		**17a** (5)	
					17a′ (9)	
25	**15b**	1:8:8	1	**16b** (9)	**17b** (9)	
26	**15c**	1:8:8	1	**16c** (t)	**17c** (9)	

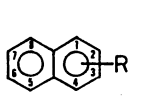
a) Naphthalene: malonic acid: manganese(III) acetate. b) Yields based on the amount of naphthalene consumed. c) The reaction was carried out at 70°C. d) The reaction was carried out at 100°C.

interaction of manganese(III) acetate and nitromethane. Recently, we have found the spiroannulation of alkenes by the use of a malonic acid-manganese(III) acetate system.[6] Fristad and Hershberger suggested that dicarboxymethyl radicals, $\cdot CH(CO_2H)_2$, produced in the oxidation system participated in this spiroannulation.[7] In connection with these manganese(III) acetate oxidations, we tried to apply a malonic acid-manganese(III) acetate system to aromatic hydrocarbons in order to obtain aromatic lactone annulation, such as the formation of propellane[4] or di-γ-lactone.[8] When aromatic compounds were oxidized with manganese(III) acetate in the presence of malonic acid, a reaction involving dicarboxymethyl radicals actually occurred. However, no aromatic lactone annulation was observed and the dicarboxymethyl group was introduced in the aromatic ring, followed by decarboxylation to give the corresponding aldehydes or further by oxidation to yield carboxylic acids. This paper now describes the results of our investigation into this reaction as regards synthetic utility, scope, limitations, and mechanistic pathway.

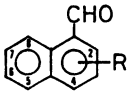
Results and Discussion

2,7-Dimethoxynaphthalene (**1a**) was selected as an aromatic substrate for the reason that the reaction products were readily separated from **1a** by TLC and could be easily characterized by spectrometry. When **1a** was oxidized with manganese(III) acetate in the presence of malonic acid under various reaction conditions (Table 1), 2,7-dimethoxy-1-naphthalenecarbaldehyde (**2a**) was obtained in moderate yield (Entries 1—7). Especially, the oxidation at a molar ratio of **1a**: malonic acid: $[Mn_3O]$=1:8:8 at reflux temperature gave **2a** in the best yield (Entry 6). Then, methoxynaphthalenes (**1b—f**) were oxidized at a molar ratio of 1:8:8 at reflux temperature, giving the corresponding naphthalenecarbaldehydes (**2b—f**) in moderate yields together with a small amount of naphthalenecarboxylic acids (**3b** and **3c**) as a by-product (Entries 8—14). The reaction of **1g** gave dicarbaldehyde (**4**) in addition to two kinds of carbaldehydes (**2g** and **2g'**) (Entry 15). In a similar oxidation of **1h**, 6,7-dimethoxy-1-naphthalenecarboxylic acid (**3h**) was mainly produced in 39% yield (Entry 16). When methylnaphthalenes (**1i—k**) and naphthalene (**1l**) were oxidized under similar reaction conditions, naphthalenecarboxylic acids (**3i—l**) were formed in 22—43% yields along with a small amount of carbaldehydes (**2i** and **2j**) and 1-(diacetoxymethyl)naphthalene (**5**) (Entries 17—20).

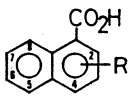
Anthracene (**6**) was oxidized with the manganese(III) acetate-malonic acid system to give four products: 9-acetoxyanthracene (**7**), 9-anthracenecarbaldehyde (**8**), 9-(diacetoxymethyl)anthracene (**9**), and 9-anthracenecarboxylic acid (**10**) (Entries 21, 22). Pyrene (**11**) also yielded an aldehyde (**12**), a diacetoxymethyl derivative (**13**), and a carboxylic acid (**14**)



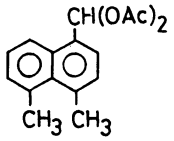
1a: R=2,7-$(CH_3O)_2$
b: R=1-CH_3O
c: R=2-CH_3O
d: R=1,5-$(CH_3O)_2$
e: R=1,3-$(CH_3O)_2$
f: R=2,6-$(CH_3O)_2$
g: R=1,7-$(CH_3O)_2$
h: R=2,3-$(CH_3O)_2$
i: R=1-CH_3
j: R=2-CH_3
k: R=1,8-$(CH_3)_2$
l: R=H
m: R=1-NO_2



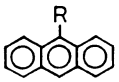
2a: R=2,7-$(CH_3O)_2$
b: R=4-CH_3O
c: R=2-CH_3O
d: R=4,8-$(CH_3O)_2$
e: R=2,4-$(CH_3O)_2$
f: R=2,6-$(CH_3O)_2$
g: R=4,6-$(CH_3O)_2$
g': R=2,8-$(CH_3O)_2$
h: R=6,7-$(CH_3O)_2$
i: R=4-CH_3
j: R=2-CH_3
4: R=5-CHO-4,6-$(CH_3O)_2$



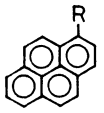
3b: R=4-CH_3O
c: R=2-CH_3O
h: R=6,7-$(CH_3O)_2$
i: R=4-CH_3
j: R=2-CH_3
k: R=4,5-$(CH_3)_2$
l: R=H



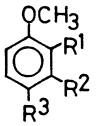
5



6: R=H
7: R=OAc
8: R=CHO
9: R=$CH(OAc)_2$
10: R=CO_2H



11: R=H
12: R=CHO
13: R=$CH(OAc)_2$
14: R=CO_2H



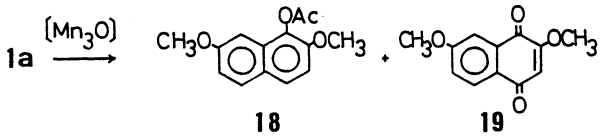
15a: $R^1=R^2=R^3=H$
b: $R^1=R^3=H$, $R^2=CH_3O$
c: $R^1=R^2=CH_3O$, $R^3=H$
16b: $R^1=H$, $R^2=CH_3O$, $R^3=CHO$
c: $R^1=R^2=CH_3O$, $R^3=CHO$
17a: $R^1=CO_2H$, $R^2=R^3=H$
a': $R^1=R^2=H$, $R^3=CO_2H$
b: $R^1=H$, $R^2=CH_3O$, $R^3=CO_2H$
c: $R^1=R^2=CH_3O$, $R^3=CO_2H$

Fig. 1.

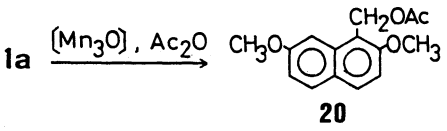
under the similar reaction conditions (Entry 23).

On the contrary, anisole (**15a**), 1,3-dimethoxybenzene (**15b**), and 1,2,3-trimethoxybenzene (**15c**) were rather inactive under these oxidation conditions to afford only a small amount of benzaldehydes (**16b** and **16c**) and benzoic acids (**17a—c**) (Entries 24—26).

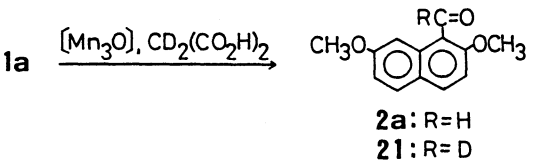
It is well-known that carboxymethyl radicals react with aromatic compounds and eventually give acetoxymethyl derivatives.[3] The acetoxymethylated products can be further oxidized with manganese(III) acetate to form diacetoxymethyl and/or formyl derivatives.[9] Aratani and Dewar have briefly reported that the oxidations of 1- and 2-methoxynaphthalene with manganese(III) acetate at 100 °C gave acetoxynaphthalenes and naphthoquinones.[10] When we repeated the oxidation of 2,7-dimethoxynaphthalene (**1a**) at a reflux temperature in which the carboxymethyl radicals could be formed more readily,[3] naphthalenecarbaldehyde, however, was not detected and the results were similar to those described in the literature (Scheme 1). Heiba and co-workers reported that a radical reaction preferentially occurred by the addition of acetic anhydride in a manganese(III) oxidation system.[3] The oxidation of **1a** was then carried out at reflux temperature under anhydrous conditions, but only acetoxymethylated product (**20**) was obtained, which was not further oxidized to give aldehyde under these reaction conditions (Scheme 2). It follows, therefore, that the formylation of aromatic compounds in the reaction of manganese(III) acetate-malonic acid system could not be caused by an attack of carboxymethyl radicals on the aromatic ring, but that malonic acid played an important role in this system. In order to clarify the source of formyl carbon, the reaction of **1a** was run by the use of malonic acid-d_4 in anhydrous benzene. As a result, a mixture of **2a** and 1-(formyl-*d*)naphthalene (**21**) was obtained in 24% yield (Scheme 3). Xanthene (**22**) was oxidized in a manganese(III) acetate-malonic acid system to give 9-(carboxymethyl)-xanthene (**23**) (Scheme 4). These facts indicate that dicarboxymethyl radicals directly attack the aromatic ring. The formation of **2a** in the reaction of **1a** with malonic acid-d_4 is probably due to a deuterium-hydrogen exchange between malonic acid-d_4 and acetic acid ligands of manganese(III) acetate. Accordingly, the mechanism for the manganese(III)-mediated formylation was depicted by the evidence mentioned above, as shown in Scheme 5, which involves double



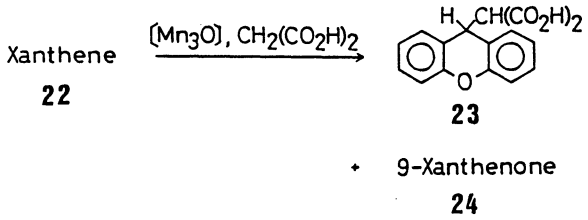
Scheme 1.



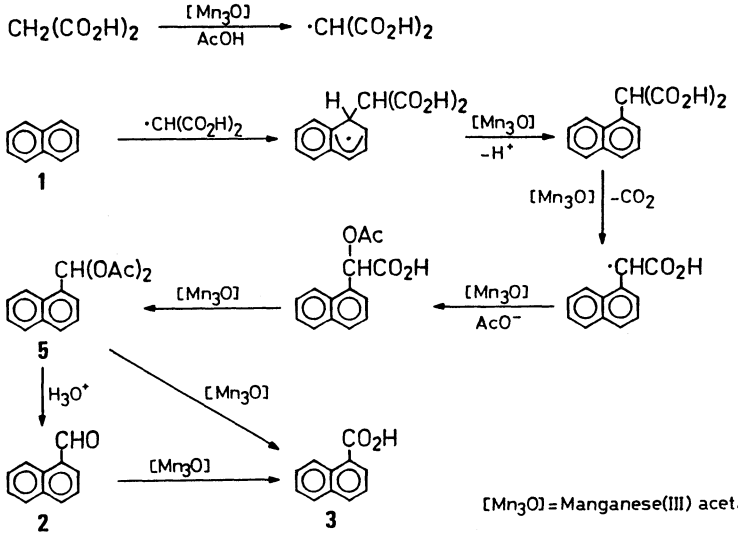
Scheme 2.



Scheme 3.



Scheme 4.



Scheme 5.

Table 2. Ionization Potentials of Aromatic Compounds and the Yields of Aldehydes and Carboxylic Acids in the Manganese(III) Oxidation

Entry	Compound	Ionization potential[a]/eV	Product(yield/%)	
			Aldehyde	Carboxylic acid
1	Anthracene (**6**)	7.36	**8**+**9** (25)	**10** (7)
2	Pyrene (**11**)	7.37	**12**+**13** (47)	**14** (10)
3	2,7-Dimethoxynaphthalene (**1a**)	7.58[b]	**2a** (59)	**3a** (0)
4	1-Methoxynaphthalene (**1b**)	7.70	**2b** (46)	**3b** (12)
5	2-Methoxynaphthalene (**1c**)	7.82	**2c** (25)	**3c** (8)
6	1,8-Dimethoxynaphthalene (**1k**)	7.92[c]	**5** (7)	**3k** (43)
7	1-Methylnaphthalene (**1i**)	7.96	**2i** (6)	**3i** (22)
8	2-Methylnaphthalene (**1j**)	8.04	**2j** (5)	**3j** (26)
9	Naphthalene (**1l**)	8.12	**2l** (0)	**3l** (29)
10	Anisole (**15a**)	8.39	**16a** (0)	**17a**+**17a'** (14)
11	1-Nitronaphthalene (**1m**)	8.59	**2m** (0)	**3m** (0)

a) Ref. 11. b) The ionization potential shows the value of **1f**. c) The ionization potential shows the value of 2,6-dimethylnaphthalene.

decarboxylation. The isolation of diacetoxymethyl derivatives (**5**, **9**, and **13**) (Table 1) would also support this mechanism. As can be seen in Fig. 1, a substituent group, such as formyl, diacetoxymethyl, or carboxyl group, is introduced at the position of the highest electron density on the aromatic ring, except for the case of 2,3-dimethoxynaphthalene (**1h**). This fact corroborates that the dicarboxymethyl radical has an electrophilic nature. Perhaps, in the case of **1h**, the attack of a bulky dicarboxymethyl radical was inhibited by a steric hindrance of the vicinal methoxyl groups. The manganese(III)-mediated formylation in the presence of malonic acid occurs preferentially to aromatic compounds which have an ionization potential in the range 7.36 to 7.82 eV (Table 2). Aromatic hydrocarbons having an ionization potential higher than these levels tend to be oxidized up to carboxylic acids, though they come to be less reactive to manganese(III) oxidation. This has been shown in cases of **1h**—**l** in which the corresponding aldehydes or diacetoxymethyl derivatives may be more readily oxidized with manganese(III) than the parent compounds. Aromatic substrates having an ionization potential over 8.4 eV could not react in this oxidation system. This aptness is similar to the direct diacetylmethylation of aromatic compounds with tris(2,4-pentanedionato)manganese(III), which is pyrolyzed in acetic acid to generate diacetylmethyl radicals.[11] The formylation of anthracene (**6**) was restrained, since a direct reaction between **6** and manganese(III) acetate via an electron-transfer mechanism took place and 9-acetoxyanthracene (**7**) was formed.[12] At this point, the behavior of **6** is seen to be different from that of **6** in direct diacetylmethylation with tris(2,4-pentanedionato)manganese(III) (only radical reaction including diacetylmethyl radicals occurs in the reaction of **6** with tris(2,4-pentanedionato)-manganese(III)).[11]

In conclusion, this manganese(III)-mediated formylation could be applied to the aromatic compounds having a relatively lower ionization potential (≦7.82 eV), although the formylation of aromatic compounds is known as Vilsmeier, Gattermann, Gattermann-Koch, Reimer-Tiemann reaction, and etc. It should be emphasized that the reaction time is extremely short (within 1 min).

Experimental

Measurements. The ^{1}H NMR spectra were measured in deuteriochloroform on a JEOL JNM-PMX60SI spectrometer at room temperature. Chemical shifts are recorded in the δ scale, relative to TMS as an internal standard. The IR spectra were taken in chloroform on a JASCO A-102 infrared spectrophotometer, and the IR spectral data are expressed in cm^{-1}. The mass spectra were obtained with a JEOL JMS-DX300 mass spectrometer at 70 eV of ionization energy. All melting points were determined with a Yanagimoto micro-melting point apparatus and were uncorrected. Thin-layer chromatography was carried out on silica gel (Wakogel B-10) with chloroform as a developing solvent.

Materials. Methoxynaphthalenes and polymethoxybenzenes were synthesized by the methylation of the corresponding naphthols and phenols with dimethyl sulfate. Naphthalene, anthracene, pyrene, and anisole were commercially available. Manganese(III) acetate was prepared by the method described in the literature.[3]

Oxidation of Aromatic Compounds with Manganese(III) Acetate in the Presence of Malonic Acid. The typical procedure for the oxidation of aromatic compounds with manganese(III) acetate in the presence of malonic acid was as follows. To a heated solution of aromatic compound (1 mmol) and malonic acid (8 mmol) in acetic acid (25 cm^3), manganese(III) acetate (1.98 g, 8 mmol for Mn(III)) was added. The mixture was heated under reflux until its dark-brown color turned opaque white. The solvent was removed in vacuo, and the residue was triturated with 2 M (1 M=1 mol dm^{-3}) HCl (25 cm^3), followed by extraction with chloroform. The chloroform extract was washed with an aqueous sodium hydrogencarbonate solution and concentrated. The aqueous solution was acidified with concentrated hydrochloric acid and subsequently extracted with ethyl acetate.

The solvent was removed in vacuo and the residue was treated with diazomethane in methanol. The neutral and esterified products, respectively, were separated on TLC. The yields are summarized in Table 1.

Oxidation Products. 2,7-Dimethoxy-1-naphthalenecarbaldehyde (2a): Mp 97.7—98.7 °C (from ethanol) (lit,[13] mp 98 °C); IR 1665 (CHO); ^{1}H NMR δ=3.86 (3H, s, OCH_3), 3.90 (3H, s, OCH_3), 6.86 (1H, d, J=9.0 Hz, H-3), 6.95 (1H, dd, J=9.0, 2.4 Hz, H-6), 7.51 (1H, d, J=9.0 Hz, H-4 or H-5), 7.78 (1H, d, J=9.0 Hz, H-5 or H-4), 8.73 (1H, d, J=2.4 Hz, H-8), and 10.75 (1H, s, CHO); MS m/z (rel intensity), 216 (100, M^+), 187 (25), 159 (53), 144 (20), 115 (31), and 102 (20). Found: C, 71.99; H, 5.59%. Calcd for $C_{13}H_{12}O_3$: C, 72.21; H, 5.59%.

6,7-Dimethoxy-1-naphthalenecarbaldehyde (2h): Mp 108—109 °C (from ethanol); IR 1682 (CHO); ^{1}H NMR δ=3.98 (3H, s, OCH_3), 4.05 (3H, s, OCH_3), 7.07 (1H, s, H-5), 7.35—8.18 (3H, m, arom. H), 8.70 (1H, s, H-8), and 10.21 (1H, s, CHO); MS m/z (rel intensity), 216 (100, M^+), 188 (37), 173 (26), and 145 (54). Found: m/z 216.0770. Calcd for $C_{13}H_{12}O_3$: M, 216.0786.

Methyl Ester of 6,7-Dimethoxy-1-naphthalenecarboxylic Acid (3h): Mp 189—190 °C (from ethanol); IR 1709 (C=O) and 1254 (C-O-C); ^{1}H NMR δ=3.96 (6H, s, 2×OCH_3), 4.00 (3H, s, OCH_3), 6.99 (1H, s, H-5), 7.20 (1H, t, J=8.0 Hz, H-3), 7.74 (1H, dd, J=8.0 and 2.4 Hz, H-4), 8.06 (1H, dd, J=8.0 and 2.4 Hz, H-2), and 8.47 (1H, s, H-8); MS m/z (rel intensity), 246 (100, M^+), 215 (41), 187 (15), 173 (20), and 145 (14). Found: m/z 246.0895. Calcd for $C_{12}H_{14}O_4$: M, 246.0891.

4,6-Dimethoxy-1,5-naphthalenedicarbaldehyde (4): Mp 185—186 °C (from ethanol); IR 1680 and 1703 (CHO); ^{1}H NMR δ=3.93 (1H, s, OCH_3), 4.00 (1H, s, OCH_3), 6.88 (1H, d, J=8.0 Hz, H-3), 7.40 (1H, d, J=9.0 Hz, H-7), 7.76 (1H, d, J=8.0 Hz, H-2), 9.41 (1H, d, J=9.0 Hz, H-8), 10.09 (1H, s, CHO), and 10.61 (1H, s, CHO); MS m/z (rel intensity), 244 (100, M^+), 229 (20), 213 (30), 199 (15), 115 (55), and 102 (40). Found: C,68.57; H, 5.02%. Calcd for $C_{14}H_{12}O_4$: C, 68.84; H, 4.95%.

1-Diacetoxymethyl-4,5-dimethylnaphthalene (5): Mp 130.4—131.4 °C (from light petroleum); IR 1240 (O-CO), 1760 (OAc); ^{1}H NMR δ=2.10 (6H, s, 2×OAc), 2.90 (6H, s, 2×CH_3), 7.1—7.5 (3H, m), 7.52 (1H, d, J=8.0 Hz), 8.09 (1H, dd, H-8), and 8.16 (1H, s, -CH<). Found: C, 71.43; H, 6.42%. Calcd for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34%.

4-Methoxy-1-naphthalenecarbaldehyde (2b) (lit,[14] mp 34 °C); **2-methoxy-1-naphthalenecarbaldehyde (2c),** mp 82.2—83.1 °C (lit,[15] mp 82.0—83.5 °C); **4,8-dimethoxy-1-naphthalenecarbaldehyde (2d),** mp 126.8—127.6 °C (lit,[16] mp 126 °C); **2,4-dimethoxy-1-naphthalenecarbaldehyde (2e),** mp 161.8—162.3 °C (lit,[17] mp 161—162 °C); **2,6-dimethoxy-1-naphthalenecarbaldehyde (2f),** mp 90.3—90.8 °C (lit,[13] mp 90 °C); **4,6-dimethoxy-1-naphthalenecarbaldehyde (2g),** mp 103.5—104.4 °C (lit,[18] mp 104 °C); **2,8-dimethoxy-1-naphthalenecarbaldehyde (2g')** (lit,[18] mp 90 °C); **4-methyl-1-naphthalenecarbaldehyde (2i),** liquid (lit,[19] bp 160—165 °C/1.3×10^3 Pa); **2-methyl-1-naphthalenecarbaldehyde (2j),** mp 50—51 °C (lit,[20] mp 51.5—52 °C); **methyl esters of 4-methoxy-1-naphthalenecarboxylic acid (3b);**[21] **2-methoxy-1-naphthalenecarboxylic acid (3c)** (lit,[22] mp 52—53 °C); **4-methyl-1-naphthalenecarboxylic acid (3i)** (lit,[23] bp 192—194 °C/1.6×10^3 Pa); **2-methyl-1-naphthalenecarboxylic acid (3j)** (lit,[23] bp 168—170 °C/2×10^3 Pa); **4,5-dimethyl-1-naphthalenecarboxylic acid (3k)**[24] and **1-naphthalenecarboxylic acid (3l)** (lit,[25] bp 100—102 °C/5.3 Pa) were characterized by its ^{1}H NMR, IR spectrum, and by comparison of the melting point or the boiling point with those of literatures.

1-Acetoxyanthracene (7): Pale yellow needles (from ethanol), mp 132—133 °C (lit,[26] mp 134—135 °C); IR 1765 (OAc); ^{1}H NMR δ=2.59 (3H, s, OAc), 7.2—8.1 (8H, m, arom. H), and 8.31 (1H, s, H-10).

9-Anthracenecarbaldehyde (8): Mp 103.5—104.5 °C (from ethanol) (lit,[27] mp 104—105 °C).

9-Diacetoxymethylanthracene (9): Mp 138—139 °C (from ethanol); IR 1760 (OAc); ^{1}H NMR δ=2.08 (6H, s, 2×OAc), 7.18—8.80 (8H, m, arom. H), 8.48 (1H, s, H-10), and 9.25 (1H, s, -CH<); MS m/z (rel intensity), 308 (14, M^+), 206 (100), 178 (95), and 151 (29). Found: m/z 308.0955. Calcd for $C_{19}H_{16}O_4$: M, 308.1048.

1-Pyrenecarbaldehyde (12): Mp 125.5—126.5 °C (from ethanol) (lit,[28] mp 127 °C).

1-Diacetoxymethylpyrene (13): Mp 151—152 °C (from ethanol); IR 1761 (OAc); ^{1}H NMR δ=2.10 (6H, s, 2×OAc), 7.27—8.76 (9H, m, arom. H), and 9.21 (1H, s, -CH<); MS m/z (rel intensity), 332 (17, M^+), 230 (35), 201 (36), and 181 (100). Found: m/z 332.1048. Calcd for $C_{21}H_{16}O_4$: M, 332.1048.

Methyl Ester of 1-Pyrenecarboxylic Acid (14): Mp 100—101 °C (from ethanol) (lit,[29] mp 101—102 °C).

The structures for the benzaldehydes (**16b, c**) and the methyl esters of 9-anthracenecarboxylic acid (**10**) (lit,[30] mp 297—298 °C), benzoic acids (**17a, a', b, c**) were determined by the analyses of their IR and ^{1}H NMR spectral data.

Oxidation of 2,7-Dimethoxynaphthalene (1a) with Manganese(III) Acetate. A modified procedure of Aratani and Dewar[10] was used for the oxidation of **1a** with manganese(III) acetate. A mixture of **1a** (1 mmol) and manganese(III) acetate (4 mmol for Mn(III)) was heated under reflux for 13 min in acetic acid (25 cm^3). The solvent was removed in vacuo and the residue was triturated with 2 M HCl (30 cm^3). The aqueous solution was extracted with chloroform and the obtained products were purified on TLC to give 1-acetoxy-2,7-dimethoxynaphthalene (**18**, 25%) and 2,7-dimethoxy-1,4-naphthoquinone (**19**, 39%). These compounds have the same spectral properties as those in the literature.[10]

Oxidation of 2,7-Dimethoxynaphthalene (1a) with Manganese (III) Acetate in the Presence of Acetic Anhydride. A mixture of **1a** (1 mmol), manganese(III) acetate (4 mmol for Mn(III)), and acetic anhydride (40 mmol) was heated under reflux for 4 min in acetic acid (25 cm^3). The reaction mixture was treated with the method described above to yield 1-(acetoxymethyl)-2,7-dimethoxynaphthalene (**20**, 54%).[3]

Reaction of 2,7-Dimethoxynaphthalene (1a) with Manganese(III) Acetate in the Presence of Malonic Acide-d_4. A mixture of **1a** (1 mmol), malonic acid (4 mmol), and manganese(III) acetate (4 mmol for Mn(III)) was heated under reflux for 12 h in dry benzene (25 cm^3) instead of acetic acid. After the work-up, **2a** was obtained in a 23% yield. Then, a similar reaction was carried out in the presence of malonic acid-d_4 instead of malonic acid to afford a mixture of **2a** (12%) and 1-(formyl-d)-2,7-dimethoxynaphthalene (**21**, 12%).

Oxidation of Xanthene (22) with Manganese(III) Acetate in the Presence of Malonic Acid. To a heated solution of xanthene (**22**, 1 mmol) and malonic acid (4 mmol) in acetic acid (25 cm^3), manganese(III) acetate (4 mmol for Mn(III)) was added. The mixture was heated under reflux for 1 min. The solvent was removed off and the residue was treated with

2 M HCl (25 cm^3). The aqueous solution was extracted with chloroform, which was subsequently washed with aqueous sodium hydrogencarbonate solution. The aqueous solution was acidified with concentated hydrochloric acid and then extracted with ethyl acetate. The acidic products obtained was methylated with diazomethane in methanol. The neutral and esterified products were separated on TLC to give a dimethyl ester of 9-dicarboxymethylxanthene (**23**, 20%) and 9-xanthenone (**24**, 6%).

Dimethyl Ester of 23: IR 1735, 1755 (OAc); ^{1}H NMR δ=3.53 (6H, s, 2×OCH_3), 3.54 (1H, d, J=8.4 Hz, -CH<), 4.83 (1H, d, J=8.4 Hz, -CH<), 6.89—7.43 (8H, m, arom.H); MS m/z (rel intensity), 312 (8, M^+), 196 (33), 181 (98), 168 (29), 139 (20), and 82 (100). Found: m/z 312.0988. Calcd for $C_{18}H_{16}O_5$: M, 312.0997.

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