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Direct Diacetylmethylation of Aromatic Compounds with Tris-(2,4-pentanedionato)manganese(III)

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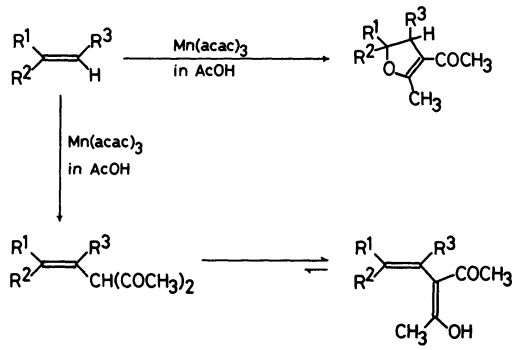
The oxidation of naphthalenes with tris(2,4-pentanedionato)manganese(III) in acetic acid gave diacetylmethyl derivatives in good to moderate yields. Using excess amounts of the oxidant, the acetylmethyl-substituted naphthalenes were further oxidized and 3-acetoxy-3-naphthyl-2,4-pentanediones were obtained. The similar oxidation of anthracenes also produced (diacetylmethyl)anthracenes together with diacetylmethylene derivatives which were further oxidized. It was found that this direct diacetylmethylation was effective when the ionization potential of the aromatic compound was lower than 8.12 eV, and that the diacetylmethyl radical which was generated directly by the thermolysis of tris(2,4-pentanedionato)manganese(III) has an electrophilic nature based on the result of the oxidation of substituted naphthalenes. The reaction pathway for the oxidation of anthracene is also discussed.

Tris(2,4-pentanedionato)manganese(III), $Mn(acac)_3$, is a well-known catalyst in polymerization, autoxidation, and peroxide reactions.[1] However, the use as an oxidant itself is rare in the literature, although the oxidative coupling reaction of phenols[2] or thiols[3] and the oxidative intramolecular cyclization of phenolic oximes[4] have been reported. Recently, the present author has found that the oxidation of olefins with $Mn(acac)_3$ gave dihydrofurans in good yields.[5] This reaction has been explained as follows. Manganese(III) complexes generally tend to undergo a rapid exchange of ligands in a donor solvent such as acetic acid which can complex manganese(III) ions,[5] and therefore, $Mn(acac)_3$ will be easily decomposed in acetic acid to form diacetylmethyl radical, $\cdot CH(COCH_3)_2$. The attack of the $\cdot CH(COCH_3)_2$ radical on olefins and subsequent oxidative cyclization afforded dihydrofurans. In the case of 9-benzylidene-9,10-dihydroanthracene, the corresponding dihydrofuran was not obtained, but one of the methylenic hydrogens of the starting olefin was replaced by the $\cdot CH(COCH_3)_2$ radical (Scheme 1).[5] This led to the present investigation of



Scheme 1.

the reaction of aromatic compounds with $Mn(acac)_3$ in the hope that direct diacetylmethylation may take place. As for the similar reaction using manganese(III) complex, it is well-known that olefins are oxidized with manganese(III) acetate to give γ-lactones in good yields,[6] while the oxidation of aromatic compounds with manganese(III) acetate afforded carboxymethyl, acetoxymethyl,[7] diacetoxymethyl,[8] and carboxy derivatives.[9] These manganese(III) acetate oxidations involve the carboxymethyl radical, $\cdot CH_2CO_2H$.[7] In this paper, the author describes a new direct diacetylmethylation of aromatic compounds with $Mn(acac)_3$.

Results

When 2-methoxynaphthalene (**1a**) was oxidized with four molar equivalents of $Mn(acac)_3$ in acetic acid at 100 °C, the reaction was completed within 13 min to give **2a** (Table 1, Entry 1). The product **2a** showed a parent ion peak at m/z 256 in the mass spectrum and a broad absorption band in the IR spectrum which could be assigned to an enolized β-diketone. The ^1H NMR spectrum of **2a** indicated the presence of a 1-acetyl-2-hydroxy-1-propenyl group and an AB quartet (J=9.0 Hz) due to aromatic protons. Consequently, this spectroscopic evidence supported the structure of **2a** being 1-(1-acetyl-2-hydroxy-1-propenyl)-2-methoxynaphthalene. The reaction of **1a** with $Mn(acac)_3$ in another solvent, such as CH_3CN, did not occur.

Oxidation of 1-methoxynaphthalene (**1b**) under the same reaction conditions produced **3b** together with a diacetylmethyl derivative **2b** (Table 1, Entry 2). The structure of **3b** was determined to be 4-(1-acetoxy-1-acetyl-2-oxopropyl)-1-methoxynaphthalene on the basis of the spectral data. The ^{13}C-off-resonance decoupling of **3b** collapsed the peak at δ=102.613 (C-2) to a doublet, but the peak at δ=120.369 (C-4) did not collapse. This shows that the 1-acetoxy-1-acetyl-2-oxopropyl group was introduced at the C-4 position. Moreover, the position of the substituent group was also supported by comparing its ^1H NMR spectrum with that of **1b**. When this reaction was carried out at a molar ratio of 1:10 at reflux temperature, **3b** was obtained as the sole product (Table 1, Entry 3).

2,7-Dimethoxynaphthalene (**1c**) was oxidized with four molar equivalents of $Mn(acac)_3$ to give (acetylmethyl)naphthalene **2c**, while a nearly equimolar mixture of **2c** and **3c** was obtained in a 1:10 molar ratio reaction (Table 1, Entries 4 and 5). It was con-

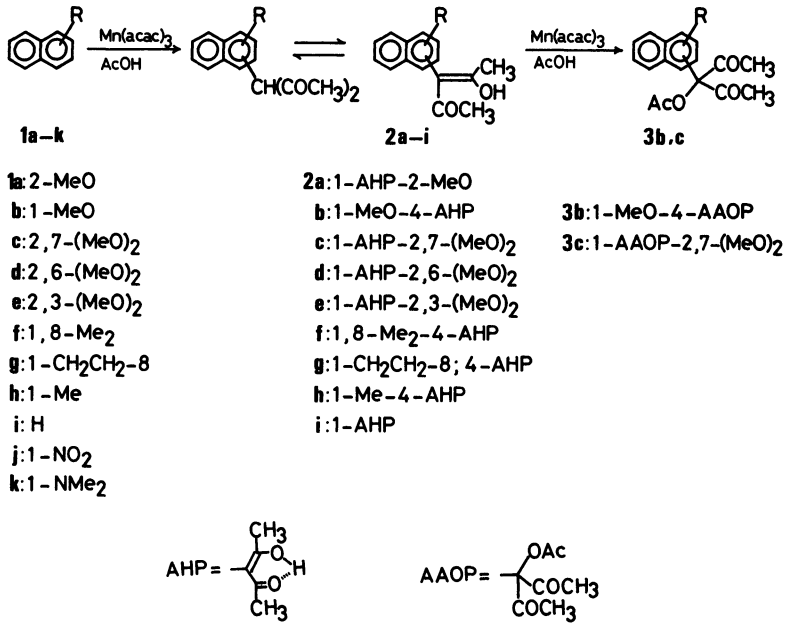


Fig. 1. Oxidation of naphthalenes (**1a—k**) with $Mn(acac)_3$ in AcOH at 100 °C.

Table 1. Oxidation of Naphthalenes with $Mn(acac)_3$ in Acetic Acid at 100 °C

Entry	Compound	Molar ratio of substrate : $Mn(acac)_3$	Time / min	Product (yield/%)[a]
1	**1a**	1 : 4	13	**2a** (54)
2	**1b**	1 : 2	10	**2b** (9) **3b** (40)
3[b]	**1b**	1 : 10	2	**3b** (62)
4	**1c**	1 : 4	15	**2c** (52)
5	**1c**	1 : 10	25	**2c** (36) **3c** (31)
6	**1d**	1 : 4	14	**2d** (46)
7	**1e**	1 : 4	10	**2e** (41)
8	**1f**	1 : 4	14	**2f** (30)
9	**1g**	1 : 4	13	**2g** (24)
10	**1h**	1 : 4	15	**2h** (15)
11	**1i**	1 : 4	15	**2i** (8)
12	**2c**	1 : 2	3	**3c** (50)

a) The yields are based on the amount of the substrate consumed. b) The reaction was carried out at the reflux temperature.

firmed that the product **3c** was derived from the further oxidation of **2c** with $Mn(acac)_3$ since the diacetylmethyl derivative **2c** was oxidized under the same reaction conditions to give only the pentanedione **3c** (Table 1, Entry 12).

The oxidations of 2,6-dimethoxynaphthalene (**1d**), 2,3-dimethoxynaphthalene (**1e**), 1,8-dimethylnaphthalene (**1f**), acenaphthene (**1g**), 1-methylnaphthalene (**1h**), and naphthalene (**1i**) with $Mn(acac)_3$ were also carried out in acetic acid to yield the corresponding diacetylmethyl derivatives (**2d—i**) (Table 1, Entries 6—11). The reaction of 1-nitronaphthalene (**1j**) with $Mn(acac)_3$ did not occur under these conditions and **1j** was recovered. 1-Dimethylaminonaphthalene (**1k**) was oxidized with $Mn(acac)_3$ under the same reaction conditions to give intractable tarry materials and no diacetylmethylated products were detected.

Anthracene (**4**) gave four products (**5**, **6**, **7**, and **8**) (Table 2, Entries 1 and 2). The products **5** and **6** were determined to be anthracenes substituted by diacetylmethyl groups in their enol forms. The **7** showed characteristic carbonyl absorptions of diacetylmethyl group in the IR spectrum, and its ^1H NMR spectrum revealed an AB quartet (J=10.2 Hz) due to four protons which were assigned to methine protons of 9,10-dihydroanthracene and diacetylmethyl group. Therefore, the structure of **7** was considered to be 9,10-bis(diacetylmethyl)-9,10-dihydroanthracene. The spectroscopic data of **8** supported the symmetrical structure of 9,10-bis(diacetylmethylene)-9,10-dihydroanthracene which seemed to be formed by the further oxidation of **6** or **7**.

Acridine (**9**), xanthene (**11**), and pyrene (**17**) were oxidized with $Mn(acac)_3$ to give corresponding diacetylmethyl derivatives in good to moderate yields (Table 2, Entries 5, 6, 8, and 9). In the oxidation of

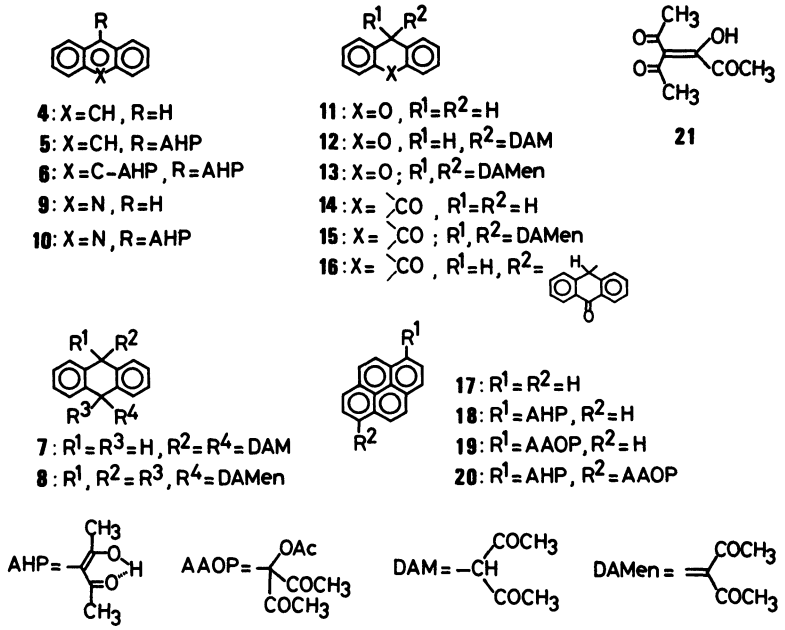


Fig. 2. Aromatic substrates and their oxidation products.

Table 2. Oxidation of Aromatic Compounds (**4**, **9**, **11**, **14**, and **17**) with $Mn(acac)_3$ in Acetic Acid at 100°C

Entry	Compound	Molar ratio of Substrate $Mn(acac)_3$	Time min	Product (yield/%)[a]
1	**4**	1:2	2	**5** (47) **6** (11) **7** (4) **8** (5)
2[b]	**4**	1:4	10	**5** (22) **6** (27) **7** (4) **8** (22)
3	**9**	1:4	14	**10** (49)
4	**11**	1:2	5	**12** (71) **13** (21)
5	**14**	1:4	19	**15** (7) **16** (78)
6	**17**	1:2	3	**18** (45) **19** (24) **20** (6)
7	**17**	1:4	8	**18** (35) **19** (23) **20** (24)

a) The yields are based on the amount of the substrate consumed. b) The reaction was carried out at the reflux temperature.

anthrone (**14**), however, a diacetylmethylene derivative **15** was obtained in poor yield, and a major product was a dimeric compound **16**. It has been reported that the product **16** was also obtained by the oxidation of **14** with manganese(III) acetate in acetic acid.[11b]

Discussion

The oxidation of aromatic compounds with manganese(III) acetate was studied in detail by Dewar et al.[10] and Heiba et al.[7] Methoxynaphthalenes (**1a** and **1b**) and anthracene (**4**) were oxidized with manganese(III) acetate in acetic acid to give naphthoquinones[10b,c] and anthraquinone,[11] respectively. These reactions were explained by the electron-transfer mechanism.[10] On the other hand, it is well-known that the free-radical mechanism involving the carboxymethyl radical, $\cdot CH_2CO_2H$, simultaneously competes with the electron-transfer process in the manganese(III) acetate–acetic acid system.[7] The attack of $\cdot CH_2CO_2H$ radicals on the aromatic ring and further oxidation mainly produces acetoxymethyl derivatives, $Ar\text{-}CH_2OAc$. Heiba and his co-workers proposed that the electron-transfer mechanism in the manganese(III) acetate–acetic acid system was observed only with aromatic compounds such as anthracene and 2-methylnaphthalene, having ionization potentials less than 8.0 eV.[7] It is also well-known that γ-lactones are obtained in good yields, when the $\cdot CH_2CO_2H$ radicals add to alkenes followed by oxidative cyclization. For this lactone annulation, it has been confirmed by subsequent experiments[12] that the lower ionization potential cutoff for useful alkenes was 8.2 eV; below this level the electron-transfer process occurred competitively. Accordingly, the free-radical mechanism in the manganese(III) acetate oxidation is characteristic for aromatic compounds and alkenes having ionization potential higher than about 8 eV.

The ionization potentials of the aromatic compounds used in this $Mn(acac)_3$ oxidation[13] and the total yields of their diacetylmethylated products are summerized in Table 3. As can be seen from this Table,

Table 3. Ionization Potentials of Aromatic Compounds and the Yields of Their Diacetylmethylated Products

Entry	Compound	Ionization potential / eV	Diacetylmethylated product yield/%[e]
1	Anthracene (**4**)	7.36[a]	75
2	Pyrene (**17**)	7.37[a]	82
3	2,6-Dimethoxynaphthalene (**1d**)	7.58[b]	46
4	1-Dimethylaminonaphthalene (**1k**)	7.59[c]	0[f]
5	1-Methoxynaphthalene (**1b**)	7.70[d]	62
6	2-Methoxynaphthalene (**1a**)	7.82[d]	54
7	1-Methylnaphthalene (**1h**)	7.96[b]	15
8	Naphthalene (**1i**)	8.12[a]	8
9	Anisole	8.39[d]	0[g]
10	1-Nitronaphthalene (**1j**)	8.59[d]	0[h]

a—d) Ref. 13. e) Total yields. f) An intractable mixture was obtained. g) No diacetylmethylated products were detected. h) This reaction did not occur and the starting material was recovered (see Experimental).

Table 4. Oxidation of Diacetylmethylated Products with $Mn(acac)_3$ in Acetic Acid at 100 °C

Entry	Compound	Molar ratio of Subsrate:$Mn(acac)_3$	Time / min	Product (yield/%)[a]	Recovery / %
1	**5**	1:2	2	**6** (40) **8** (24)	29
2	**6**	1:2	2	**8** (66)	33
3	**7**	1:2	2		100
4	**7**	1:4	6	**8** (18)	77
5	**12**	1:2	2	**13** (29)	68

a) The yields are based on the amount of the substrated used.

it has been proved that the diacetylmethylation was effective when ionization potential of the aromatic compound was lower than 8.12 eV. This behavior as an oxidant is in contrast to that of manganese(III) acetate and it shows that $Mn(acac)_3$ is a weaker oxidant than manganese(III) acetate. The reason why the reaction of 1-dimethylaminonaphthalene (**1k**) with $Mn(acac)_3$ did not give any diacetylmethylated products in spite of the ionization potential was low is that a lone-pair electron on the nitrogen atom is more liable to be abstracted by $Mn(acac)_3$ than a π-electron of the aromatic ring, and then, another side-reaction such as polymerization might ensue.[15]

The existence of the $\cdot CH(COCH_3)_2$ radical in this reaction was proved indirectly by the isolation of 3-acetyl-4-hydroxy-3-hexene-2,5-dione (**21**), since **21** must be formed by a bimolecular coupling reaction of $\cdot CH(COCH_3)_2$ radicals. The **21** was produced regardless of the substrate used in the $Mn(acac)_3$–acetic acid system, and particularly, the formation of **21** was the best when the oxidation was carried out at room temperature (see Experimental and Reference).[14]

It has been suggested that the $\cdot CH(COCH_3)_2$ radical has an electrophilic nature like the $\cdot CH_2CO_2H$ radical generated in the manganese(III) acetate–acetic acid system,[7] since the diacetylmethyl group is situated at a position ortho or para to the electron-donating group in the oxidation of naphthalenes (Table 1 and Fig. 1).

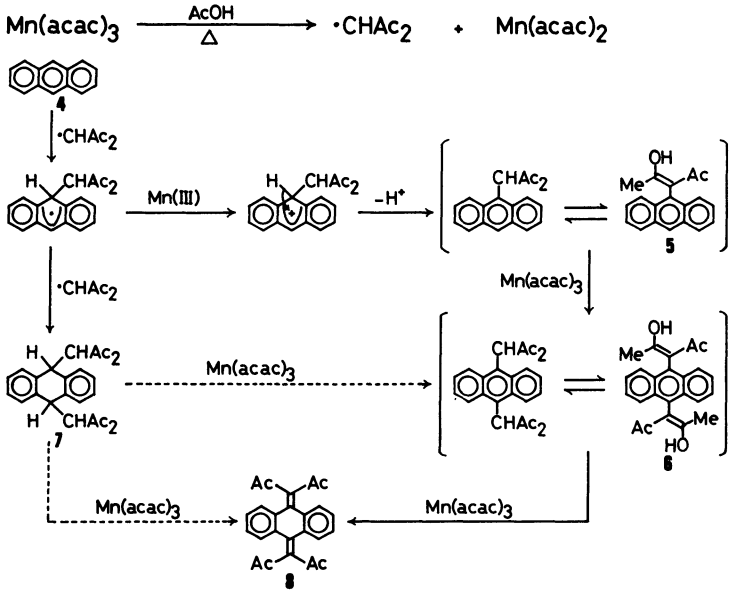
When the enol **5** was oxidized with two molar equivalents of $Mn(acac)_3$, the bis(enol) **6** and the bis(diacetylmethylene)anthracene (**8**) were obtained (Table 4, Entry 1). The oxidation of **6** under the same reaction conditions gave only **8** (Table 4, Entry 2). Although 9,10-bis(diacetylmethyl)-9,10-dihydroanthracene (**7**), on the other hand, did not react with $Mn(acac)_3$ in a molar ratio of 1:2, a small amount of **8** was formed in a molar ratio of 1:4 (Table 4, Entries 3 and 4). Therefore, the route from **7** to **8** is not important. The reaction pathway for the oxidation of anthracene (**4**) with $Mn(acac)_3$ is illustrated in Scheme 2.

Thus, it is concluded that this new direct diacetylmethylation i) takes place in $Mn(acac)_3$–acetic acid system, ii) is characteristic for aromatic compounds having ionization potential lower than about 8 eV, and iii) the $\cdot CH(COCH_3)_2$ radical involved in this oxidation system is somewhat electrophilic.

Experimental

Measurements. Melting points were determined with an Electrothermal apparatus and are uncorrected. The IR spectra were taken on a JASCO A-102 infrared spectrophotometer, and the IR spectral data are expressed in cm^{-1}. The ^1H and ^{13}C NMR spectra were recorded on a Hitachi Perkin-Elmer R-24 (60 MHz) and a JEOL FX-100 instrument at room temperature. Chemical shifts are recorded in the δ scale, relative to TMS as an internal standard. The mass spectra were obtained with a JEOL JMS-DX-300 mass spectrometer using a direct-insertion probe at an ionizing voltage of 70 eV.

Materials. $Mn(acac)_3$ was prepared by the method de-



Scheme 2.

scribed in the literature.[16] Methoxynaphthalenes (**1a—e**) were synthesized by the methylation of the corresponding naphthols with dimethyl sulfate. Other starting materials (**1f—k**, **4**, **9**, **11**, **14**, and **17**) were obtained from commercial samples from the Wako Pure Chemical Industries, Ltd.

General Procedure for the Oxidation of Aromatic Compounds with Mn(acac)$_3$. The oxidation of aromatic compound (1 mmol) with a suitable amount of Mn(acac)$_3$ (indicated in the Tables) was carried out in acetic acid (25 cm^3) at 100 °C until an opaque dark brown mixture changed to a clear brown solution. The solvent was removed in vacuo, and the residue was triturated with 2 M (1 M=1 mol dm^{-3}) HCl (25 cm^3) and then extracted with chloroform. The products were separated on TLC (Wako gel B-10), with chloroform as the developing solvent. The yields are summarized in Tables 1, 2, and 4.

Oxidation Products. 1-(1-Acetyl-2-hydroxy-1-propenyl)-2-methoxynaphthalene (2a): Colorless needles (from ethanol), mp 133.5—134.5 °C; IR ($CHCl_3$) 1620 (COC=COH) and 3300—3600 (OH); ^{1}H NMR ($CDCl_3$) δ=1.71 (6H, s, 2×CH_3), 3.88 (3H, s, OCH_3), 7.29 (1H, d, J=9.0 Hz, H-3), 7.86 (1H, d, J=9.0 Hz, H-4), 7.2—7.9 (4H, m, ArH), and 16.90 (1H, s, OH); MS m/z (rel intensity), 256 (M^+, 100), 213 (40), 169 (30), 141 (20), and 43 (50). Found: C, 74.79; H, 6.18%. Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29%.

4-(1-Acetyl-2-hydroxy-1-propenyl)-1-methoxynaphthalene (2b): Colorless needles (from methanol), mp 114.0—114.5 °C; IR ($CHCl_3$) 1610 (COC=COH) and 3300—3600 (OH); ^{1}H NMR ($CDCl_3$) δ=1.74 (6H, s, 2×CH_3), 3.96 (3H, s, OCH_3), 6.77 (1H, d, J=8.4 Hz, H-2), 7.17 (1H, d, J=8.4 Hz, H-3), 7.30—8.40 (4H, m, ArH), and 16.80 (1H, s, OH). Found: C, 74.67; H, 6.25%. Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29%.

4-(1-Acetoxy-1-acetyl-2-oxopropyl)-1-methoxynaphthalene (3b): Colorless cubes (from ethanol), mp 179.5—180.0 °C; IR ($CHCl_3$) 1722 and 1749 (C=O); ^{1}H-NMR ($CDCl_3$) δ=2.223 (6H, s, 2×CH_3), 2.336 (3H, s, OAc), 4.034 (3H, s, OCH_3), 6.795 (1H, d, J=8.3 Hz, H-2), 7.373 (1H, d, J=8.3 Hz, H-3), and 7.258—8.400 (4H, m, ArH); ^{13}C NMR ($CDCl_3$)[17] δ=20.827 (q, CH_3), 27.525 (q, 2×CH_3), 55.665 (q, OCH_3), 95.359 (s, >C<), 102.613 (d, C-2), 120.369 (s, C-4), 122.826 (d, C-8), 124.903 (d, C-7), 125.664 (d, C-6), 126.775 (s, C-8a), 126.980 (d, C-3), 127.536 (d, C-5), 132.128 (s, C-4a), 157.080 (s, C-1), 170.330 (s, C=O), and 200.810 (s, 2×C=O); MS m/z (rel intensity), 314 (M^+, 10), 272 (20), 230 (50), 158 (30), and 43 (100). Found: C, 68.83; H, 5.81%. Calcd for $C_{18}H_{18}O_5$: C, 68.78; H, 5.77%.

1-(1-Acetyl-2-hydroxy-1-propenyl)-2,7-dimethoxynaphthalene (2c): Colorless needles (from methanol), mp 120.0—120.5 °C; IR ($CHCl_3$) 1624 (COC=COH) and 3300—3600 (OH); ^{1}H NMR ($CDCl_3$) δ=1.77 (6H, s, 2×CH_3), 3.83 (3H, s, OCH_3), 3.88 (3H, s, OCH_3), 6.93—7.78 (3H, m, ArH), 7.15 (1H, d, J=9.6 Hz, H-3), 7.79 (1H, d, J=9.6 Hz, H-4), and 16.87 (1H, s, OH). Found: C, 71.16; H, 6.31%. Calcd for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34%.

1-(1-Acetoxy-1-acetyl-2-oxopropyl)-2,7-dimethoxynaphthalene (3c): Colorless needles (from ethanol), mp 176—177 °C; IR ($CHCl_3$) 1723 and 1760 (C=O); ^{1}H NMR ($CDCl_3$) δ=2.25 (9H, s, 2×CH_3 and OAc), 3.88 (3H, s, OCH_3), 3.92 (3H, s, OCH_3), 7.03 (1H, dd, J=9.0 and 2.4 Hz, H-6), 7.13 (1H, d, J=9.0 Hz, H-3), 7.39 (1H, d, J=2.4 Hz, H-8), 7.71 (1H, d, J=9.0 Hz, H-5), and 7.86 (1H, d, J=9.0 Hz, H-4). Found: C, 66.23; H, 5.96%. Calcd for $C_{19}H_{20}O_6$: C, 66.27; H, 5.85%.

1-(1-Acetyl-2-hydroxy-1-propenyl)-2,6-dimethoxynaphthalene (2d): Colorless prisms (from ethanol), mp 134—135 °C; IR ($CHCl_3$) 1620 (COC=COH) and 3300—3600 (OH); ^{1}H NMR ($CDCl_3$) δ=1.75 (6H, s, 2×CH_3), 3.88 (6H, s, 2×OCH_3), 7.0—7.7 (3H, m, ArH), 7.25 (1H, d, J=9.6 Hz, H-4), 7.78 (1H, d, J=9.6 Hz, H-5), and 16.89 (1H, s, OH). Found: C, 71.07; H, 6.39%. Calcd for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34%.

1-(1-Acetyl-2-hydroxy-1-propenyl)-2,3-dimethoxynaphthalene (2e): Colorless needles (from methanol), mp 117—118 °C; IR ($CHCl_3$) 1600 (COC=COH) and 3300—3600 (OH); ^{1}H NMR ($CDCl_3$) δ=1.77 (6H, s, 2×CH_3), 3.89 (3H, s, OCH_3), 3.97 (3H, s, OCH_3), 6.91 (1H, s, H-4), 7.05—7.80 (4H, m, ArH), and 16.88 (1H, s, OH). Found: C, 71.10; H, 6.37%. Calcd for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34%.

4-(1-Acetyl-2-hydroxy-1-propenyl)-1,8-dimethylnaphthalene (2f): Colorless needles (from methanol), mp 149—150 °C; IR ($CHCl_3$) 1605 (COC=COH) and 3300—3600 (OH); ^{1}H NMR ($CDCl_3$) δ=1.750 (6H, s, 2×CH_3), 2.965 (6H, s, 2×CH_3), 7.151 (1H, d, J=7.1 Hz, H-2 or 3), 7.284 (1H, d, J=7.1 Hz, H-3 or 2), 7.275—7.734 (3H, m, ArH), and 16.70 (1H, s, OH); ^{13}C NMR ($CDCl_3$)[17] δ=23.762 (q, 2×CH_3), 26.161

(q, CH_3), 26.249 (q, CH_3), 113.125 (s, $\succ C=$), 124.328 (d, C-3 or 6), 125.762 (d, C-6 or 3), 128.511 (d, C-5), 129.243 (d, C-2 or 7), 129.798 (d, C-7 or 2), 133.045 (s, C-8a), 133.689 (s, C-4), 134.830 (s, C-4a), 136.000 (s, C-1 or 8), 136.175 (s, =C-O and C-8 or 1), 191.519 (s, C=O). Found: C, 80.06; H, 7.13%. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13%.

5-(1-Acetyl-2-hydroxy-1-propenyl)acenaphthene (2g): Colorless needles (from methanol), mp 141.5—142.5 °C; IR ($CHCl_3$) 1603 (COC=COH) and 3100—3600 (OH); ^{1}H NMR ($CDCl_3$) δ=1.79 (6H, s, 2×CH_3), 3.40 (4H, s, 2×CH_2), 7.17—7.47 (5H, m, ArH), and 16.79 (1H, s, OH). Found: C, 80.77; H, 6.47%. Calcd for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39%.

4-(1-Acetyl-2-hydroxy-1-propenyl)-1-methylnaphthalene (2h): Colorless plates (from methanol), mp 122 °C; IR ($CHCl_3$) 1600 (COC=COH) and 3200—3600 (OH): ^{1}H NMR ($CDCl_3$) δ=1.75 (6H, s, 2×CH_3), 2.74 (3H, s, CH_3), 7.21 (1H, d, J=7.2 Hz, H-2 or 3), 7.37 (1H, d, J=7.2 Hz, H-3 or 2), 7.20—8.11 (4H, m, ArH), and 16.80 (1H, s, OH). Found: C, 79.67; H, 6.73%. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71%.

1-(1-Acetyl-2-hydroxy-1-propenyl)naphthalene (2i): Pale orange needles (from methanol), mp 105—106 °C; IR ($CHCl_3$) 1600 (COC=COH) and 3200—3600 (OH); ^{1}H NMR ($CDCl_3$) δ=1.75 (6H, s, 2×CH_3), 7.2—8.0 (7H, m, ArH), and 16.80 (1H, s, OH). Found: C, 79.38; H, 6.25%. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24%.

9-(1-Acetyl-2-hydroxy-1-propenyl)anthracene (5): Colorless needles (from ethanol), mp 176—177 °C; IR ($CHCl_3$) 1597 (COC=COH) and 3200—3600 (OH); ^{1}H NMR ($CDCl_3$) δ=1.59 (6H, s, 2×CH_3), 7.32—8.17 (8H, m, ArH), 8.49 (1H, s, H-10), and 16.97 (1H, s, OH). Found: C, 82.43; H, 5.79%. Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84%.

9,10-Bis(1-acetyl-2-hydroxy-1-propenyl)anthracene (6): Colorless needles (from ethyl acetate), mp over 300 °C; IR ($CHCl_3$) 1598 (COC=COH) and 3200—3600 (OH); ^{1}H NMR ($CDCl_3$) δ=1.65 (12H, s, 4×CH_3), 7.51—8.22 (8H, m, ArH), and 16.98 (2H, s, 2×OH). Found: C, 76.91; H, 6.05%. Calcd for $C_{24}H_{22}O_4$: C, 76.98; H, 5.92%.

9,10-Bis(diacetylmethyl)-9,10-dihydroanthracene (7): Colorless plates (from ethanol), mp 215—216 °C; IR ($CHCl_3$) 1695 and 1735 (C=O); ^{1}H NMR ($CDCl_3$) δ=2.10 (12H, s, 4×CH_3), 4.44 (2H, d, J=10.2 Hz, H-9 and H-10), 4.89 (2H, d, J=10.2 Hz, 2×$\succ$CH-), and 7.12 (8H, s, ArH). Found: C, 76.69; H, 6.49%. Calcd for $C_{24}H_{24}O_4$: C, 76.57; H, 6.43%.

9,10-Bis(diacetylmethylene)-9,10-dihydroanthracene (8): Colorless needles (from ethanol), mp 219 °C; IR ($CHCl_3$) 1686 (C=O); ^{1}H NMR ($CDCl_3$) δ=2.27 (12H, s, 4×CH_3), and 7.24—7.56 (8H, m, ArH). Found: C, 77.34; H, 5.56%. Calcd for $C_{24}H_{20}O_4$: C, 77.40; H, 5.41%.

9-(1-Acetyl-2-hydroxy-1-propenyl)acridine (10): Pale yellow needles (from ethanol), mp 189—190 °C; IR ($CHCl_3$) 1610 (COC=COH) and 3100—3600 (OH); ^{1}H NMR ($CDCl_3$) δ=1.65 (6H, s, 2×CH_3), 7.35—8.44 (8H, m, ArH), and 17.05 (1H, s, OH). Found: C, 77.89; H, 5.60; N, 4.96%. Calcd for $C_{18}H_{15}O_2N$: C, 77.96; H, 5.45; N, 5.05%.

Oxidation of Xanthene (11). A mixture of xanthene (**11**) (364.4 mg; 2 mmol) and $Mn(acac)_3$ (1.4160 g; 4 mmol) was heated in acetic acid (25 cm^3) at 100 °C for 5 min, followed by treatment in a manner similar to that mentioned above, which gave a mixture of **12** and its enol form (263.3 mg), **13** (79.2 mg), and **11** (recovered 122.3 mg). The ratio of keto and enol was 2:1 based on the ^{1}H NMR spectrum. The mixture was recrystallized from ethanol and only the keto compound (**12**) was isolated.

9-(Diacetylmethyl)xanthene (12): Colorless needles (from ethanol), mp 142.5 °C; IR ($CHCl_3$) 1697 and 1731 (C=O); ^{1}H NMR ($CDCl_3$) keto form δ=1.84 (6H, s, 2×CH_3), 4.08 (1H, d, J=9.6 Hz, H-9), 4.84 (1H, d, J=9.6 Hz, $\succ$CH-), and 6.95—7.30 (8H, m, ArH); enol form δ=1.84 (6H, s, 2×CH_3), 5.30 (1H, s, H-9), 6.8—7.4 (8H, m, ArH), and 17.16 (1H, s, OH). Found: C, 77.20; H, 5.90%. Calcd for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75%.

9-(Diacetylmethylene)xanthene (13): Pale yellow needles (from ethanol), mp 144—145 °C; IR ($CHCl_3$) 1676 and 1706 (C=O); ^{1}H NMR ($CDCl_3$) δ=2.20 (6H, s, 2×CH_3) and 6.95—7.57 (8H, m, ArH). Found: C, 77.44; H, 5.06%. Calcd for $C_{18}H_{14}O_3$: C, 77.68; H, 5.07%.

Oxidation of Anthrone (14). 10-(Diacetylmethylene)anthrone (15): Colorless needles (from ethanol), mp 161 °C; IR ($CHCl_3$) 1669 and 1707 (C=O); ^{1}H NMR ($CDCl_3$) δ=2.22 (6H, s, 2×CH_3) and 7.5—8.4 (8H, m, ArH). Found: C, 78.59; H, 4.91%. Calcd for $C_{19}H_{14}O_3$: C, 78.60; H, 4.85%.

10,10′-Bianthrone (16): Pale yellow needles (from $CHCl_3$), mp 268—269 °C (lit, [11b] mp 230—250 °C); IR (KBr) 1657 (C=O); ^{1}H NMR ($CDCl_3$) δ=4.69 (2H, s, H-10 and 10′) and 6.70—7.98 (16H, m, ArH). Found: C, 86.91; H, 4.66%. Calcd for $C_{28}H_{18}O_2$: C, 87.02; H, 4.69%.

Oxidation of Pyrene (17). 1-(1-Acetyl-2-hydroxy-1-propenyl)pyrene (18): Pale orange needles (from ethanol), mp 158.0—158.5 °C; IR ($CHCl_3$) 1602 (COC=COH) and 3200—3600 (OH); ^{1}H NMR ($CDCl_3$) δ=1.76 (6H, s, 2×CH_3), 7.69—8.26 (9H, m, ArH), and 16.86 (1H, s, OH). Found: C, 83.87; H, 5.35%. Calcd for $C_{21}H_{16}O_2$: C, 83.98; H, 5.37%.

1-(1-Acetoxy-1-acetyl-2-oxopropyl)pyrene (19): Colorless needles (from ethanol), mp 178.0—178.5 °C; IR ($CHCl_3$) 1722 and 1749 (C=O); ^{1}H NMR ($CDCl_3$) δ=2.26 (6H, s, 2×CH_3), 2.39 (3H, s, OAc), and 7.82—8.43 (9H, m, ArH). Found: C, 76.79; H, 5.06%. Calcd for $C_{23}H_{18}O_4$: C, 77.08; H, 5.06%.

1-(1-Acetoxy-1-acetyl-2-oxopropyl)-6-(1-acetyl-2-hydroxy-1-propenyl)pyrene (20): Colorless needles (from methanol), mp 218—219 °C; IR ($CHCl_3$) 1603 (COC=COH), 1722 (C=O), 1749 (OAc), and 3300—3600 (OH); ^{1}H NMR ($CDCl_3$) δ=1.77 (6H, s, 2×CH_3), 2.26 (6H, s, 2×$COCH_3$), 2.39 (3H, s, OAc), 7.90 (1H, d, J=9.0 Hz, ArH), 7.99 (1H, d, J=9.0 Hz, ArH), 8.27 (1H, d, J=9.0 Hz, ArH), 8.47 (1H, d, J=9.0 Hz, ArH), 8.0—8.2 (4H, m, ArH), and 16.84 (1H, s, OH). Found: C, 73.46; H, 5.23%. Calcd for $C_{28}H_{24}O_6$: C, 73.67; H, 5.30%.

Oxidation of 1-Nitronaphthalene (1j). 1-Nitronaphthalene (**1j**) (198.7 mg; 1 mmol) was oxidized with $Mn(acac)_3$ (1.4298 g; 4 mmol) in acetic acid (25 cm^3) at 100 °C. The reaction was terminated after 15 min and **1j** (173.0 mg) was recovered.

Formation of 21 in the $Mn(acac)_3$ Oxidation. 1-Methoxynaphthalene (**1b**) (319.2 mg; 2 mmol) and $Mn(acac)_3$ (1.4240 g; 4 mmol) were heated at 100 °C in acetic acid (30 cm^3) for 10 min, affording **2b** (17.4 mg), **3b** (93.7 mg), and **21** (105.2 mg). The **21** was formed in all the $Mn(acac)_3$-acetic acid oxidation.

3-Acetyl-4-hydroxy-3-hexene-2,5-dione (21): Colorless prisms (from benzene), mp 115—116 °C; IR ($CHCl_3$) 1668, 1708 (C=O), and 3000—3600 (OH); ^{1}H NMR ($CDCl_3$) δ=1.607 (3H, s, CH_3), 2.389 (3H, s, CH_3), 2.605 (3H, s, CH_3), and 6.395 (1H, s, OH); ^{13}C NMR ($CDCl_3$) δ=197.558 (s, C=O), 196.910 (s, C=O), 194.919 (s, C=O), 112.959 (s, C=C), 106.294 (s, C=C), 29.648 (q, CH_3), 21.810 (q, CH_3), and 18.816 (q, CH_3); MS m/z (rel intensity), 170 (M^+, 6), 127 (80), 85 (50), 67 (100), and 43 (97). Found: C, 56.38; H, 5.95%. Calcd for $C_8H_{10}O_4$: C, 56.46; H, 5.92%.

Oxidation of 2c. The **2c** (102.2 mg; 0.36 mmol) and $Mn(acac)_3$ (258.5 mg; 0.72 mmol) were heated in acetic acid (15 cm^3) at 100 °C for 3 min. The reaction mixture was treated in a manner similar to that described above to give **3c** (29.0 mg) and **2c** (recovered 53.6 mg).

Oxidation of 5. The (diacetylmethyl)anthracene (**5**) (99.1 mg; 0.36 mmol) was oxidized with $Mn(acac)_3$ (266.4 mg; 0.72 mmol) in acetic acid (20 cm^3) at 100 °C for 2 min. After separation by TLC, **6** (53.9 mg; 40%), **8** (32.2 mg; 24%), and **5** (recovered 28.7 mg; 29%) were obtained.

Oxidation of 6. A mixture of bis(diacetylmethyl)anthracene (**6**) (103.5 mg; 0.28 mmol) and $Mn(acac)_3$ (198.2 mg; 0.56 mmol) was heated in acetic acid (20 cm^3) at 100 °C for 2 min, affording **8** (67.5 mg; 66%) and **6** (recovered 33.8 mg; 33%).

Oxidation of 7. The reaction of **7** (50.8 mg; 0.135 mmol) and $Mn(acac)_3$ (103.4 mg; 0.27 mmol) was carried out in acetic acid (10 cm^3) at 100 °C for 2 min. After work-up, however, only **7** was recovered. On the other hand, **7** (52.0 mg; 0.135 mmol) was oxidized with $Mn(acac)_3$ (199.5 mg; 0.54 mmol) in acetic acid (10 cm^3) at 100 °C for 6 min, giving **8** (9.2 mg; 18%) and **7** (recovered 40 mg; 77%).

Oxidation of 12. 9-(Diacetylmethyl)xanthene (**12**) (102.6 mg; 0.37 mmol) and $Mn(acac)_3$ (262.0 mg; 0.74 mmol) were heated on a water bath for 2 min. After the treatment described above, 9-(diacetylmethylene)xanthene **13** (29.9 mg; 29%) and **12** (recovered 69.3 mg; 68%) were obtained.

Oxidation of 1a with $Mn(acac)_3$ in CH_3CN. The reaction of **1a** (175.3 mg; 1 mmol) with $Mn(acac)_3$ (1.4146 g; 4 mmol) was carried out in CH_3CN (25 cm^3) at 100 °C for 3 h. The solvent was removed under diminished pressure and the residue was triturated with 2 M HCl (25 cm^3). The aqueous mixture was extracted with $CHCl_3$ and separated on TLC, which gave only **1a** (recovered 136.1 mg).

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