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Manganese(III)-Mediated Carbon–Carbon Bond Formation in the Reaction of Xanthenes with Active Methylene Compounds

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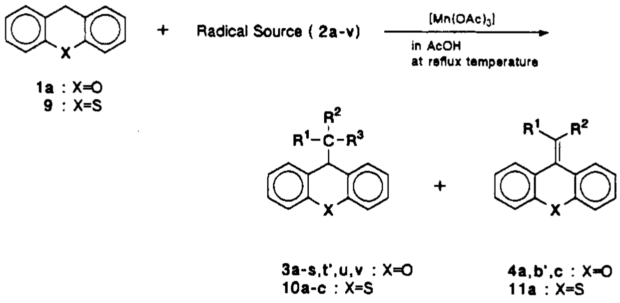
Oxidation of xanthenes with manganese(III) acetate in the presence of active methylene compounds such as 1,3-dicarbonyl compounds, malononitrile derivatives, acetone, and nitromethane selectively gives 9-substituted xanthene derivatives in good yields. A similar oxidation of thioxanthene also yields 2-(9-thioxanthenyl)-1,3-dicarbonyl compounds in 57–91% yields. The obtained 2-(9-xanthenyl)-1,3-dicarbonyl compounds are readily converted to 2-(9-xanthenylidene)-1,3-dicarbonyl derivatives using manganese(III) complexes or 2,3-dichloro-5,6-dicyano-1,4-benzoquinone. The mechanisms for the formation of 9-substituted xanthenes are discussed on the basis of the reaction of intermediates, the electron-donating substituent effect on the xanthene ring system, effect of additives, and comparison with a reaction of radical-trapping reagents.

Scheme I



1a : X=O
9 : X=S

3a-s,t',u,v : X=O
10a-c : X=S

4a,b',c : X=O
11a : X=S

a : R^1=R^2=COMe, R^3=H
b : R^1=R^2=CO_2Me, R^3=H
b': R^1=CO_2Me, R^2=CO_2H, R^3=H
c : R^1=R^2=CO_2Et, R^3=H
d : R^1=R^2=$CONH_2$, R^3=H
e : R^1=R^2=COPh, R^3=H
f : R^1=R^2=CO(4-$MeOC_6H_4$), R^3=H
g : R^1=COMe, R^2=COPh, R^3=H
h : R^1=COPh, R^2=CO_2Et, R^3=H
i : R^1=COMe, R^2=CO_2Et, R^3=H
j : R^1=CO_2Me, R^2=$COCH_2CO_2Me$, R^3=H
k : R^1=CO_2Et, R^2=$COCH_2CO_2Et$, R^3=H
l : R^1=R^2=CN, R^3=H
m : R^1=CN, R^2=$CONH_2$, R^3=H
n : R^1=CN, R^2=CO_2Et, R^3=H
o : R^1=R^2=CO_2H, R^3=H
p : R^1=R^2=CO_2Me, R^3=Cl
q : R^1=R^2=CO_2Me, R^3=Br
r : R^1=R^2=CO_2Et, R^3=Me
s : R^1=R^2=CO_2Et, R^3=CH_2Ph
t : R^1=Ph, R^2=CN, R^3=H
t' : R^1=Ph, R^2=$CONH_2$, R^3=H
u : R^1=COMe, R^2=R^3=H
v : R^1=NO_2, R^2=R^3=H

Introduction

Recently, manganese(III) acetate has been widely used for the carbon–carbon bond formation in organic synthesis.[1] The manganese(III) acetate, abbreviated as [$Mn(OAc)_3$] hereafter, is known as a one-electron oxidant. When anthracene, fluorene, and 2-methoxynaphthalene are oxidized with [$Mn(OAc)_3$] in acetic acid, anthraquinone, 9-fluorenone,[2] and 2-methoxy-1,4-naphthoquinone[3] are produced, respectively. On the other hand, reactions of alkenes having ionization potentials higher than 8.2 eV with [$Mn(OAc)_3$] yield γ-lactones.[4] It is said that the carboxymethyl radical, $^{\bullet}CH_2CO_2H$, which is directly produced by the thermolysis of [$Mn(OAc)_3$], participates in the lactonization.[5] Aromatic hydrocarbons, which have ionization potentials higher than 8.0 eV, can also react with carboxymethyl radicals,[6] and the corresponding carboxymethylation, acetoxymethylation,[7] or carboxylation[8] occurs. When acetone,[9] nitromethane,[10] or 1,3-dicarbonyl compounds are present in the [$Mn(OAc)_3$] oxidation system, the corresponding α-oxo radicals are formed which react with alkenes[11] and aromatic hydrocarbons[12] similarly to the carboxymethyl radicals. There are not very many investigations of these radicals themselves, such as carboxymethyl radicals and α-oxo radicals, because the radicals are very active, and only acetic acid, which is a protic medium, has been used as a solvent.[13] In order to trap these radicals, the oxidation of 1,3-dicarbonyl compounds such as 2,4-pentanedione with [$Mn(OAc)_3$] was carried out in the presence of xanthene which might be a good radical-trapping reagent in the manganese(III) oxidation system.[12a] As a result, the corresponding 1,3-dicarbonyl groups were actually introduced in the benzylic position of xanthene in fairly good yields. However, we found that 1,3-dicarbonyl radicals did not attack xanthenyl radical, but xanthene was directly oxidized by [$Mn(OAc)_3$] to give xanthylium ions or 9-acetoxyxanthene which underwent

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[1] For reviews, see: (a) de Klein, W. J. in *Organic Syntheses by Oxidation with Metal Compounds*; Mijs, W. J., De Jonge, C. R. H. I., Eds.; Plenum: New York, 1986; pp 261-314. (b) Arndt, D. *Manganese Compounds as Oxidizing Agents in Organic Chemistry*; Open Court: La Salle, 1981; pp 1-25. (c) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidation of Organic Compounds*; Academic: New York, 1981.

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[13] Manganese(III) acetate is soluble only in hot carboxylic acids.

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Table I. Reaction of Xanthene (1a) with Various Radical Sources in the Presence of Manganese(III) Acetate[a]

entry	radical source	reaction time, min	convn of 1a, %	product (yield, %)[b]				
1	$CH_2(COMe)_2$ (**2a**)	1	76	**3a** (34)	**4a** (34)			
2	$CH_2(CO_2Me)_2$ (**2b**)	23	100	**3b** (65)				**7a** (11)
3	$CH_2(CO_2Et)_2$ (**2c**)	26	100	**3c** (72)		**5a** (7)		
4	$CH_2(CONH_2)_2$ (**2d**)	3	100	**3d** (81)		**5a** (4)		
5	$CH_2(COPh)_2$ (**2e**)	6	90	**3e** (40)				
6	$CH_2\{CO(4\text{-}MeOC_6H_4)\}_2$ (**2f**)	3	77	**3f** (42)			**6f** (11)	
7	$CH_2(COMe)COPh$ (**2g**)	1	85	**3g** (46)				
8	$CH_2(COPh)CO_2Et$ (**2h**)	3	89	**3h** (42)				
9	$CH_2(COMe)CO_2Et$ (**2i**)	2	76	**3i** (45)		**5a** (3)		
10	$CH_2(CO_2Me)COCH_2CO_2Me$ (**2j**)	3	69	**3j** (42)[c]				
11	$CH_2(CO_2Et)COCH_2CO_2Et$ (**2k**)	1	61	**3k** (22)[c]				
12	$CH_2(CN)_2$ (**2l**)	2	70	**3l** (22)		**5a** (4)		
13	$CH_2(CN)CONH_2$ (**2m**)	2	87	**3m** (46)		**5a** (13)		
14	$CH_2(CN)CO_2Et$ (**2n**)	2	86	**3n** (28)		**5a** (11)		
15	$CH_2(CO_2H)_2$ (**2o**)	4	58	**3o** (21)[d]				**7o** (24)[d]
16	$Cl\text{-}CH(CO_2Me)_2$ (**2p**)	3	89	**3p** (56)				
17	$Br\text{-}CH(CO_2Me)_2$ (**2q**)	10	100	**3q** (53)				
18	$Me\text{-}CH(CO_2Et)_2$ (**2r**)	8	81	**3r** (9)		**5a** (29)		
19	$PhCH_2\text{-}CH(CO_2Et)_2$ (**2s**)	11	84	**3s** (6)		**5a** (20)		
20	$PhCH_2CN$ (**2t**)	125	88	**3t′** (19)[e]		**5a** (20)		
21	MeCOMe (**2u**)	8	81	**3u** (3)		**5a** (43)		
22	$MeNO_2$ (**2v**)	32	70	**3v** (25)		**5a** (45)		
23	$BrCH(CO_2H)_2$ (**2w**)	4	37	(complex mixture)				
24	$PhCH(CO_2Et)_2$ (**2x**)	5	52				**6x** (15)	
25	none	150	81			**5a** (72)		
26	Ac_2O	126	71			**5a** (66)		**8** (3)[f]
27[g]	**2a**	4	93	**10a** (60)	**11a** (24)			
28[g]	**2b**	45	100	**10b** (57)		**12** (15)		
29[g]	**2c**	52	100	**10c** (68)		**12** (11)		

[a] The reaction was carried out in boiling acetic acid at the molar ratio of **1a** (1 mmol):**2a–x**:$[Mn(OAc)_3]$ = 1:4:4, except for the case of **2j** (1:4:8). [b] Isolated yield based on the amount of **1a** used, except for **6f** and **6x**. [c] The product was obtained as a 1:1 keto–enol mixture. [d] The yield was calculated as the corresponding methyl ester. [e] The cyano group of **3t** was hydrolyzed during the oxidation to give the corresponding acetamide (**3t′**). [f] The product **8** was obtained as a mixture of three regioisomers. [g] Thioxanthene (**9**) was used as a radical-trapping reagent instead of **1a**.

benzylic nucleophilic substitution by the anions of 1,3-dicarbonyl compounds complexed to Mn(II) acetate, although the corresponding 1,3-dicarbonyl radicals were certainly formed in a side reaction. In this report we discuss the synthesis of 9-substituted xanthene derivatives using manganese(III) acetate and the reaction mechanism.

Results

Reaction of Xanthene (1a) with $[Mn(OAc)_3]$ in the Presence of Various Active Methylene Compounds. Heiba and Dessau reported that the reaction 2-phenylpropene with $[Mn(OAc)_3]$ in the presence of 2,4-pentanedione quantitatively gave 3-acetyl-2,5-dimethyl-5-phenyl-4,5-dihydrofuran, and they postulated that the dihydrofuran was produced via a free-radical mechanism involving the diacetylmethyl radical, $^{\bullet}CH(COMe)_2$.[14,15] Therefore, we examined the 2,4-pentanedione–$[Mn(OAc)_3]$ system as the first step. A mixture of xanthene (**1a**) and 2,4-pentanedione (**2a**) was heated in glacial acetic acid, and $[Mn(OAc)_3]$ was added just before refluxing. The reaction was over in 1 min, and 3-(9-xanthenyl)-2,4-pentanedione (**3a**) and 3-(9-xanthenylidene)-2,4-pentanedione (**4a**) were obtained after the usual workup. Increasing the molar ratio of $[Mn(OAc)_3]$ resulted in an increasing yield of **3a** and **4a** (Figure 1). However, using excess amounts of $[Mn(OAc)_3]$ caused overoxidation such as the conversion of **3a** to **4a**.[12a] Accordingly, the optimum molar ratio of **1a**:**2a**:$[Mn(OAc)_3]$ = 1:4:4 was determined on the basis of Figure 1. The reaction of various active methylene compounds, i.e., 1,3-dicarbonyl compounds (**2b–k,o–s,w,x**), malononitriles (**2l–n**), benzyl cyanide (**2t**), acetone (**2u**), and nitromethane (**2v**), were conducted under similar reaction conditions, and the corresponding 9-substituted xanthene derivatives were formed. The results are summarized in Scheme I and Table I. In some cases, **1a** was oxidized directly with $[Mn(OAc)_3]$ to give 9-xanthenone

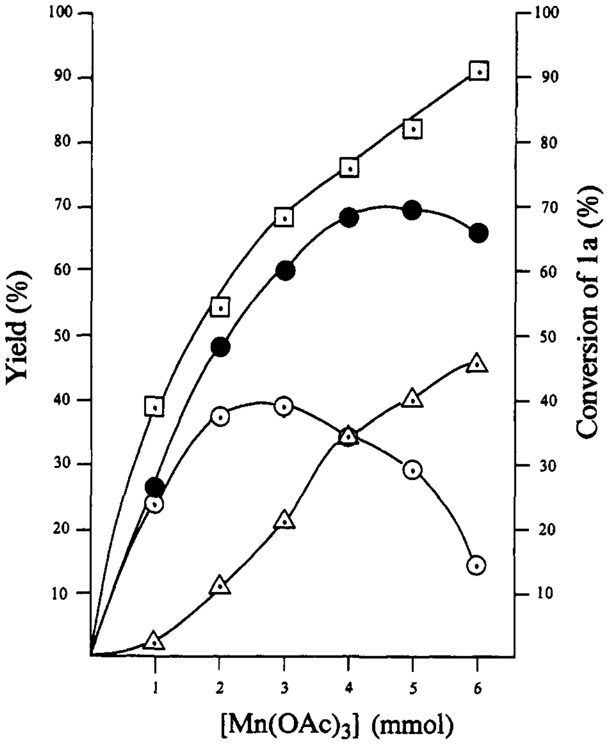

Figure 1. Yields of radical-trapped products (**3a** and **4a**) and conversion of xanthene (**1a**) in the reaction of **1a** (1 mmol) with 2,4-pentanedione (**2a**, 4 mmol) in the presence of $[Mn(OAc)_3]$: (○) **3a**, (△) **4a**, (●) **3a** + **4a**, (□) conversion of **1a**.

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Table II. Reaction of Xanthenes (1a–e) with 2,4-Pentanedione (2a) or Methyl Malonate (2b) in the Presence of Manganese(III) Acetate[a]

entry	xanthene	radical source	reaction time, min	convn of 1a–f, %	product (yield, %)[b]			
1	**1a**	**2a**	1	76	**3a** (34)	**4a** (34)		
30	**1b**	**2a**	1	79	**3ab** (44)	**4ab** (28)		
31[c]	**1c**	**2a**	1	93	**3ac** (36)	**4ac** (35)	**5c** (4)	
32	**1d**	**2a**	1	100	**3ad** (54)	**4ad** (18)		
33[d]	**1e**	**2a**	7	100	**3ae** (29)	**4ae** (45)		
2	**1a**	**2b**	8	98	**3b** (65)			**7a** (11)
34	**1b**	**2b**	8	97	**3bb** (63)			**7b** (19)
35	**1c**	**2b**	3	98	**3bc** (62)	**4bc** (3)	**5c** (2)	**7c** (14)

[a] The reaction was carried out in boiling glacial acetic acid at the molar ratio of **1a–e** (1 mmol):**2a** or **2b**:[Mn(OAc)$_3$] = 1:4:4. [b] Isolated yield based on the amount of **1a–e** used. [c] The reaction was conducted at the molar ratio of **1c** (1 mmol):**2a**:[Mn(OAc)$_3$] = 1:4:5. [d] The reaction was carried out at 70 °C in glaical acetic acid.

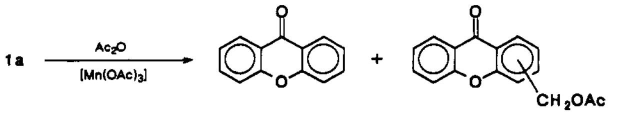
Table III. Effect of Additives for the Reaction of Xanthene (1a) with 2,4-Pentanedione (2a) or Methyl Malonate (2b) in the Presence of Manganese(III) Acetate[a]

entry	radical source	additive, mmol	reaction time, min	convn of 1a, %	product (yield, %)[b]			
1	**2a**	none	1	76	**3a** (34)	**4a** (34)		
36	**2a**	LiCl (10)	2	54	**3a** (45)	**4a** (8)		
37	**2a**	Ac_2O (100)	1	74	**3a** (32)	**4a** (33)		
38	**2a**	H_2O (200)	1	86	**3a** (41)	**4a** (31)	**5a** (7)	
39	**2a**	H_2O (400)	1	92	**3a** (49)	**4a** (30)	**5a** (8)	
40	**2a**	H_2O (800)	1	96	**3a** (58)	**4a** (19)	**5a** (17)	
41	**2a**	H_2O (1600)	1	100	**3a** (61)	**4a** (14)	**5a** (22)	
42	**2a**	$Cu(OAc)_2$ (2)	1	73	**3a** (25)	**4a** (27)	**5a** (16)	
43	**2a**	oxygen[c]	1	71	**3a** (30)	**4a** (20)	**5a** (18)	
44	**2a**	argon[d]	1	85	**3a** (31)	**4a** (45)		
2	**2b**	none	8	98	**3b** (65)			**7a** (11)
45	**2b**	H_2O (200)	8	93	**3b** (53)		**5a** (21)	**7a** (14)
46	**2b**	H_2O (400)	10	95	**3b** (52)		**5a** (25)	**7a** (12)
47	**2b**	H_2O (800)	90	97	**3b** (51)	**4b′** (9)[e]	**5a** (23)	**7a** (5)
48	**2b**	H_2O (1600)	120	97	**3b** (37)	**4b′** (11)[e]	**5a** (21)	**7a** (3)

[a] The reaction was carried out in boiling glacial acetic acid at the molar ratio of **1a** (1 mmol):**2a** or **2b**:[Mn(OAc)$_3$] = 1:4:4. [b] Isolated yield based on the amount of **1** used. [c] The reaction was carried out under an oxygen atmosphere. [d] The reaction was conducted under an argon atmosphere. [e] One ester group of **4b** was hydrolyzed under the reaction conditions to give the corresponding monoester (**4b′**).

(**5a**) and the radicals formed from **2f** and **2x** reacted *head-to-head* to afford the corresponding dimers, 2,3-bis(4-methoxybenzoyl)-1,4-bis(4-methoxyphenyl)-1,4-butanedione (**6f**) and tetraethyl 1,2-diphenyl-1,1,2,2-ethanetetracarboxylate (**6x**). Nitroethane, ethyl phenylacetate, 2,5-hexanedione, ethyl levulinate, and acetonitrile, did not react with **1a**, but **5a** was obtained (see the Experimental Section). The reaction using **2w** gave a complex mixture, and no products were isolated.

It has been considered that [Mn(OAc)$_3$] decomposes in boiling glacial acetic acid to produce carboxymethyl radicals,[6] and adding acetic anhydride to the reaction mixture increases the production of the carboxymethyl radicals[6] and/or acetic anhydride radicals, $^{\bullet}CH_2CO_2COMe$.[4,16] In order to examine the reaction with these radicals, the reaction of **1a** with [Mn(OAc)$_3$] was carried out in the absence of an active methylene compound and in the presence of acetic anhydride. Contrary to our expectation, no radical-substituted products at the 9-position of **1a** were formed, but **5a** and a small amount of acetoxymethylated 9-xanthenone (**8**) were obtained (entries 25, 26).[8]



5a **8**

Reaction of Thioxanthene (9) with 1,3-Dicarbonyl Compounds in the Presence of [Mn(OAc)$_3$]. Since **9** is readily available from the reduction of thioxanthone (**12**) and **9** can be expected to have results similar to **1a**, we examined the reaction of **9** and 1,3-dicarbonyl compounds (**2a–c**) in the presence of [Mn(OAc)$_3$]. Reactions similar to those of **1a** occurred and the desired products (**10a-c** and **11a**) were obtained, along with **12** (see Scheme I and Table I, entries 27–29).

Reaction of Substituted Xanthenes (1b–e) with 2,4-Pentanedione (2a) or Dimethyl Malonate (2b) in the Presence of [Mn(OAc)$_3$]. In order to examine the electronic effect on the xanthene skeleton, the similar reactions of 3-methoxyxanthene (**1b**), 3,6-dimethoxyxanthene (**1c**), 1-methoxyxanthene (**1d**), and 1,3,6-trimethoxyxanthene (**1e**) with **2a** or **2b** were conducted. The results are summarized in Scheme II and Table II. In both series of **1b–e** reacting with **2a** and **2b**, the total yields of the substituted products (**3** + **4**, **3** + **7**, or **3** + **4** + **7**) were slightly higher than that in the case of **1a**. The reactions of **1c** also afforded a small amount of 3,6-dimethoxy-9-xanthenone (**5c**).

Effect of Additives for the Reaction of Xanthene (1a) with 2,4-Pentanedione (2a) or Dimethyl Malonate (2b) in the Presence of [Mn(OAc)$_3$]. It is known that the oxidation using [Mn(OAc)$_3$] is sometimes affected by additives such as acetic anhydride,[4,5,6,16] potassium acetate,[6] chloride ion,[17] copper(II) acetate,[18] or water.[19] Some ad-

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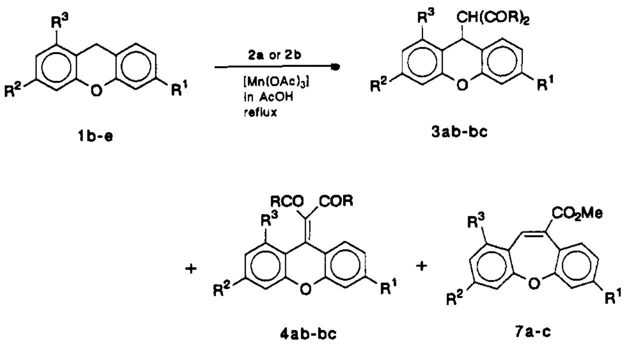
Scheme II

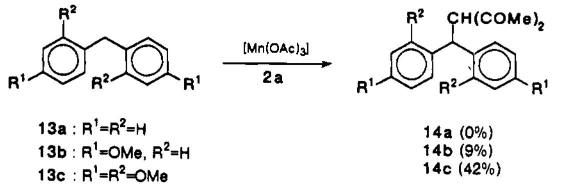


a : R^1=R^2=R^3=H
b : R^1=OMe, R^2=R^3=H
c : R^1=R^2=OMe, R^3=H
d : R^1=R^2=H, R^3=OMe
e : R^1=R^2=R^3=OMe

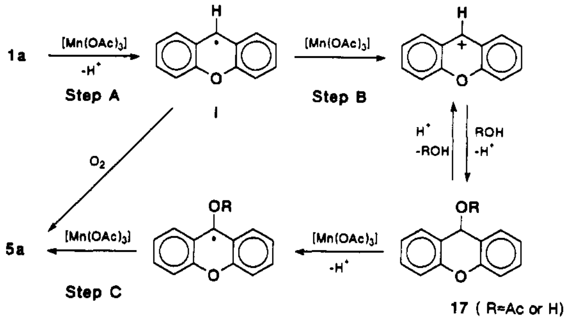
ab : R^1=OMe, R^2=R^3=H, R=Me
ac : R^1=R^2=OMe, R^3=H, R=Me
ad : R^1=R^2=H, R^3=OMe, R=Me
ae : R^1=R^2=R^3=OMe, R=Me
bb : R^1=OMe, R^2=R^3=H, R=OMe
bc : R^1=R^2=OMe, R^3=H, R=OMe

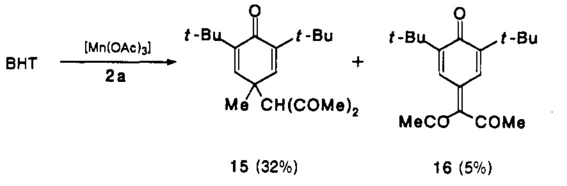
ditives promote the radical reactions in some cases while others inhibit them, and the reverse cases can also happen. In order to elucidate the effects of additives in the present reactions, the reactions of **1a**–**2a** or **1a**–**2b** with [Mn(OAc)$_3$] were run under various reaction conditions in the presence of additives (Table III). Lithium chloride, acetic anhydride, copper(II) acetate, and oxygen depressed the total production of **3a** and **4a** (entries 36, 37, 42, and 43). On the other hand, adding water to the reaction of **1a**–**2a** increased the conversion of **1a** and the total yield **3a** and **4a**, although a considerable amount of **5a** also formed when water concentration was increased (entries 38–41). The reaction of **1a**–**2b** in the presence of water significantly decreased the total yield of the corresponding substituted products (**3b**, **4b′**, **7a**) and a considerable amount of **5a** was formed (entries 45–48).

Reaction of Radical-Trapping Reagents with 2,4-Pentanedione (2a) in the Presence of [Mn(OAc)$_3$]. In order to explore possible radical-trapping reagents in the present reaction system, the reactions of aromatic compounds analogous to **1a** were attempted. When the reaction of fluorene with **2a** was performed under the same conditions, 9-acetoxyfluorene (12%) was only formed. The similar reactions of 9,10-dihydroacridine and 9,10-dihydro-10-methylacridine gave intractable mixtures, and only acridine (54%) was isolated from the reaction of 9,10-dihydroacridine. In the reactions of 9,10-dihydroanthracene and acridine with **2a**, small amounts of the corresponding radical-trapped products were obtained. Dibenzosuberone, triptycene, and diphenylmethane (**13a**) did not react with **2a** under these reaction conditions. However, the introduction of methoxyl groups to the phenyl group in **13a** caused the similar reaction of **1a** to produce **14b** and **14c**. When 2,6-di-*tert*-butyl-4-methylphenol (BHT), a well-known radical-trapping agent, was used instead of **1a**, the products **15** and **16** were formed.[20] Adding water to the reaction system increased the production of **15** (from 32% to 65%). However, the reaction of BHT with **2b** yielded a complex mixture, and no radical-trapped products were isolated.



Scheme III





Oxidation of Substituted Xanthene Derivatives (3a–c). The oxidation of **3a**–**c** was performed in order to confirm the dehydrogenation of **3** to **4** during the present reaction process. It was found that the oxidation of **3a** with [Mn(OAc)$_3$] actually gave **4a** (31%), and using [Mn(OAc)$_3$]–**2a** or [Mn(acac)$_3$] as an oxidant was sufficient for the conversion of **3a** to **4a** (56%). However, [Mn(OAc)$_3$] was not adequate for the oxidation of **3b** (5–12%). On the other hand, the reaction of **3a**–**c** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) as dehydrogenating agent quantitatively gave **4a**–**c** (92–94%).

Discussion

It is believed that the lactonization of alkenes and the acetoxymethylation of aromatic hydrocarbons using [Mn(OAc)$_3$] are caused by carboxymethyl radicals, $^{\bullet}CH_2CO_2H$, which must be formed by the direct thermal decomposition of [Mn(OAc)$_3$].[4,5,6,19] However, the oxidation of xanthene (**1a**) with [Mn(OAc)$_3$] in the absence of an active methylene compound did not give any radical-trapped products, but did produce 9-xanthenone (**5a**) (Table I, entry 25 and Scheme III). This shows that an electron-transfer reaction occurred because of the lower ionization potential of **1a** (I = 8.04 eV).[21] Accordingly, **1a** was directly oxidized with [Mn(OAc)$_3$] similar to the reaction of anthracene, acenaphthene, and fluorene.[2,22] The stoichiometry of the reaction requires 4 equiv of [Mn(OAc)$_3$] per equivalent of **1a**, and the reaction is likely to proceed via an intermediate (**17**: R = Ac or H). Indeed, 9-hydroxyxanthene (**17**: R = H) was oxidized with [Mn(OAc)$_3$] to give **5a** (see the Experimental Section). On the other hand, it was reported that the direct diacetylmethylation of an aromatic ring using [Mn(acac)$_3$] was effective when the ionization potential of the aromatic compound was lower than 8.12 eV.[12a] In the [Mn(acac)$_3$] oxidation system, diacetylmethyl group is efficiently con-

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[18] (a) Anderson, J. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1970**, *92*, 2450. (b) Kochi, J. K.; Subramanian, R. V. *J. Am. Chem. Soc.* **1965**, *87*, 4855. Kochi, J. K.; Bemis, A.; Jenkins, C. L. *Ibid.* **1968**, *90*, 4616.

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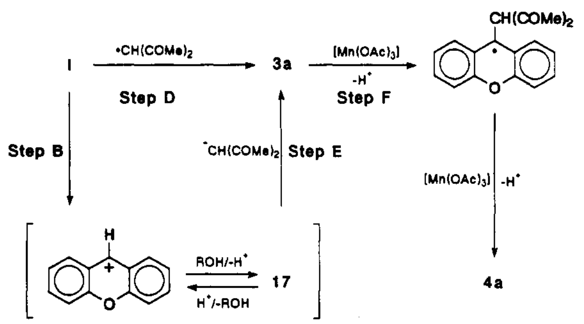
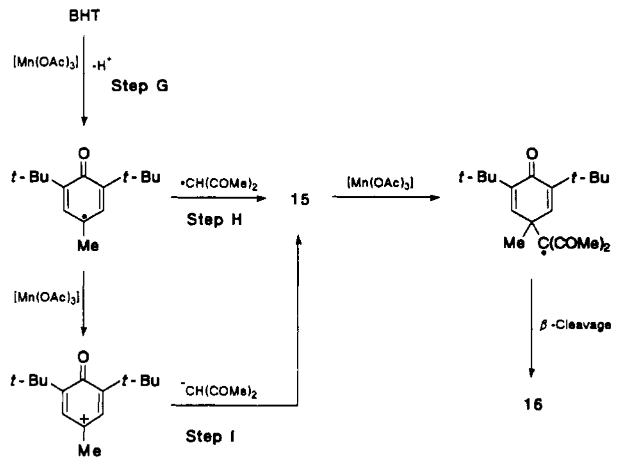
[22] Cremonesi, P.; Cavalieri, E. L.; Rogan, E. G. *J. Org. Chem.* **1989**, *54*, 3561.

Scheme IV



Scheme V



nected not to the aromatic rings of **1a**, but at the benzylic position (C-9). This peculiar reaction is reminiscent of the oxidation of 4-methoxytoluene (I = 8.18 eV) previously noted by Dewar et al.[3,23] and the oxidation of toluene (I = 8.82 eV)[24] reported by Heiba et al.[6] The former gives 4-methoxybenzyl acetate via an electron-transfer process and the latter affords (acetoxymethyl)toluenes which are produced by radical pathways involving carboxymethyl radicals. Since the ionization potential of **1a** is lower than that of 4-methoxytoluene, it is thought that the electron-transfer mechanism was operative for **1a** in the absence of an active methylene compound and **5a** was actually obtained. On the other hand, when active methylene compounds are present in the oxidation system of **1a**, the reaction occurs at the benzylic position of **1a** at first just as in the case of 4-methoxytoluene and then the active methylene group is introduced at the C-9 position. However, any radicals such as diacetylmethyl radicals and carboxymethyl radicals are not substituted on the aromatic ring, probably because the reactions are too slow to occur.

It is thought that there are two pathways for the formation of 9-substituted xanthenes (Scheme IV). One is diacetylmethyl radicals produced by the oxidation of **2a** with [Mn(OAc)$_3$] attack 9-xanthenyl radicals (**I**) (step D) and the other is that either xanthylium ion or the intermediate **17** undergoes benzylic nucleophilic substitution by diacetylmethyl anions complexed to Mn(II) or Mn(III) acetate (step E).[25] In order to determine the reaction pathway, a reaction of **17** with **2a** in the presence of manganese(II) acetate was carried out in boiling glacial acetic acid for 1 min and **3a** was quantitatively obtained after general workup (see the Experimental Section). Furthermore, the addition of water to the reaction of **1a** with **2a** in the presence of [Mn(OAc)$_3$] remarkably influenced the yield of **3a** (Table III, entries 38–41). Therefore, these results support step E. On the other hand, the reaction of BHT with **2a** actually gave radical-trapped products (**15** and **16**). In addition, a competition reaction of **2a** in the presence of **1a** and BHT was conducted in refluxing glacial acetic acid for 1 min to give **3a** (27%), **4a** (33%), **15** (67%), and **16** (6%). For BHT, however, to function as an efficient radical-trapping reagent in this system requires the presence of water. These results suggest that nucleophilic substitution (steps E and I) occurs rather than radical reaction (steps D and H), although we could not neglect the direct connection of diacetylmethyl radicals to xanthenyl radicals (**I**) since head-to-head radical coupling compounds (**2f** and **2x**) were isolated as a byproduct from the same reaction mixture.

Thioxanthene (**9**; I = 7.84 eV)[21] and methoxyxanthenes (**1b–e**), which seem to have lower ionization potentials[26] than **1a**, favor step A. However, the ability of carbon–carbon bond formation at C-9 is similar to that of **1a**.

Copper(II) acetate is especially prone to oxidize alkyl radicals such as **I** rather than [Mn(OAc)$_3$];[18] that is, addition of copper(II) acetate to the reaction system accelerates steps B and C. Thus it was observed that **5a** was formed and the yields of **3a** and **4a** decreased (entry 42). The alkyl radical (**I**) can also be intercepted by molecular oxygen. Thus, the reaction of **1a** with [Mn(OAc)$_3$]–**2a** in the presence of an oxygen atmosphere afforded **5a**, which could be directly attributed to a peroxy intermediate such as **17** (R = OH)[28] (entries 43 and 44). It is known that chlorination of organic compounds preferentially occurs when chloride ion is added to the [Mn(OAc)$_3$] oxidation system.[17] However, the addition of lithium chloride to the present reaction did not occur the corresponding chlorination (entry 36).

3-(9-Xanthenylidene)-2,4-pentanedione (**4a**) is formed even at a reactant molar ratio of 1:2, although 2 equiv of [Mn(OAc)$_3$] is ordinarily enough for the production of **3a** (Figure 1). Two more equivalents of [Mn(OAc)$_3$] ought to be needed for the formation of **4a** from **3a** (Scheme IV). This is supported by the oxidation of **3a** with [Mn(OAc)$_3$] shown in Table IV (supplementary material). However, it is also suggested that hydrogen abstraction by the diacetylmethyl radical participates in step F (entries 50 and 51 in Table IV). Using DDQ for the conversion of **3** to **4** is significantly more efficient than using [Mn(OAc)$_3$], and this is expected for the synthetic application of 3-(9-xanthenylidene)-2,4-pentanediones.

In closing, we have demonstrated that this manganese(III)-mediated reaction may have a synthetic utility for xanthenyl and xanthenylidene derivatives, and that the C–C bond formation of this reaction may occur via nucleophilic substitution of 1,3-dicarbonyl anions after oxidation of xanthenes with [Mn(OAc)$_3$].

Experimental Section

Instrumentation. ^{1}H and ^{13}C NMR spectra were measured in chloroform-d, DMSO-d_6, or carbon tetrachloride on either a

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[23] Andrulis, P. J., Jr.; Dewar, M. J. S.; Dietz, R.; Hunt, R. L. *J. Am. Chem. Soc.* **1966**, *88*, 5473. Andrulis, P. J., Jr.; Dewar, M. J. S. *Ibid.* **1966**, *88*, 5483.

[24] Howell, J. O.; Goncalves, J. M.; Amatore, C.; Klasinc, L.; Wightman, R. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3968.

[25] One of the referees suggested the nucleophilic substitution pathway.

[26] Ionization potentials of methoxyxanthenes (**1b–e**) can be estimated to be under 7.75 eV on the basis of comparing naphthalene with methoxynaphthalenes or anisole with methoxyanisoles.[27]

[27] Bock, H.; Wabner, G.; Kroner, J. *Chem. Ber.* **1972**, *105*, 3850.

[28] van Helden, R.; Kooyman, E. C. *Recl. Trav. Chim. Pays-Bas* **1961**, *80*, 57. Bartlett, P. D.; Traylor, T. G. *J. Am. Chem. Soc.* **1963**, *85*, 2407. Factor A.; Russell, C. A.; Traylor, T. G. *Ibid.* **1965**, *87*, 3692.

JEOL JNM-PMX60SI or a JNM-EX90 spectrometer at room temperature. Chemical shifts are reported in ppm downfield from an internal TMS standard. Infrared spectra were recorded in chloroform or KBr on a JASCO A-102 spectrometer. The IR spectral data are expressed in cm^{-1}. Mass spectra were measured on either a JEOL JMS-01 SG-2, a JEOL JMS-DX300, or a SIMAZU GCMS QP1000 mass spectrometer at an ionizing voltage of 70 eV. All melting points were determined with a Yanagimoto micromelting point apparatus and were uncorrected. Elemental analyses were performed by the Elemental Analysis Center, Faculty of Science, Kyushu University, Japan.

Oxidation of Xanthene (1a) with [Mn(OAc)$_3$] in the Presence of Various Radical Sources (2a–x). A typical procedure for the oxidation of **1a** with [Mn(OAc)$_3$] in the presence of an active methylene compound was as follows. A mixture of **1a** (1 mmol), radical source (**2a–x**) (4 mmol), and glacial acetic acid (30 mL) was heated in a 100-mL round-bottomed flask. Just before refluxing, [Mn(OAc)$_3$] (4 mmol) was added to the mixture. The mixture was continually heated under reflux until the brown color of [Mn(OAc)$_3$] turned colorless or pale yellow. The solvent was removed in vacuo, and the residue was triturated with 2 M (1 M = 1 mol dm^{-3}) hydrochloric acid (30 mL) and then extracted with chloroform. The products were separated on TLC (Wakogel B-10) with chloroform as the developing solvent. The reaction times and the yields are summarized in Table I.

3-(9-Xanthenyl)-2,4-pentanedione (3a): colorless needles (from EtOH); mp 147–148 °C (lit.[12a] mp 142.5 °C).

3-(9-Xanthenylidene)-2,4-pentanedione (4a): yellow needles (from EtOH); mp 145–146 °C (lit.[12a] mp 144–145 °C).

Dimethyl (9-xanthenyl)malonate (3b): yellow needles (from MeOH/H$_2$O); mp 59–61 °C; IR (CHCl$_3$) ν 1755, 1734 (C=O); ^{1}H NMR (CCl$_4$) δ 3.43 (6 H, s, 2 OMe), 3.46 (1 H, d, J = 9.0 Hz, –CH<), 4.74 (1 H, d, J = 9.0 Hz, –CH<), 6.52–7.83 (8 H, m, arom H); MS m/z (rel intensity), 312 (M$^+$, 8), 252 (3), 221 (6), 196 (33), 181 (98), 168 (29), 139 (20), 82 (100); found m/z 312.0988, calcd for C$_{18}$H$_{16}$O$_5$ M, 312.0998.

10-(Methoxycarbonyl)dibenz[*b,f*]oxepin (7a): colorless needles (from EtOH); mp 91.3–92.0 °C; IR (CHCl$_3$) ν 1710 (C=O); ^{1}H NMR (CDCl$_3$) δ 3.90 (3 H, s, OMe), 7.05–7.60 (8 H, m, arom H), 7.90 (1 H, s, =CH—); ^{13}C NMR (CDCl$_3$) δ 167.430 (C=O), 159.121, 158.927 (CO), 138.027, 131.658, 130.733, 130.360, 130.255, 125.034, 124.691, 121.394, 121.141 (arom CH and CH=), 131.300, 128.823, 127.690 (arom C and >C=), 52.341 (MeO). Anal. Found: C, 76.15; H, 4.79. Calcd for C$_{16}$H$_{12}$O$_3$: C, 76.18; H, 4.80.

In order to confirm the structure of **7a**, methyl (9-xanthenylidene)acetate, a structural isomer, was prepared from 9-xanthenone and methyl bromoacetate by the Reformatsky reaction.

Methyl 9-xanthenylideneacetate: pale yellow needles (from MeOH); mp 87 °C; IR (CHCl$_3$) ν 1711 (C=O); ^{1}H NMR (CDCl$_3$) δ 3.76 (3 H, s, OMe), 6.20 (1 H, s, =CH–), 7.05–8.15 (8 H, m, arom H). ^{13}C NMR (CDCl$_3$) δ 167.325 (C=O), 152.393, 151.483 (CO), 139.728 (arom C), 131.285, 130.554, 129.748, 123.960, 123.736, 122.528, 117.113, 116.815 (arom CH), 122.767 (arom C), 119.008 (>C=), 109.938 (CH=), 51.357 (MeO).

1,3-Diphenyl-2-(9-xanthenyl)-1,3-propanedione (3e): pale yellow needles (from EtOH/H$_2$O); mp 113 °C; IR (CHCl$_3$) ν 1691, 1664 (C=O); ^{1}H NMR (CDCl$_3$) δ 5.35 (1 H, d, J = 9.0 Hz, –CH<), 5.76 (1 H, d, J = 9.0 Hz, –CH<), 6.67–7.83 (18 H, m, arom H). Anal. Found: C, 83.17; H, 4.96. Calcd for C$_{28}$H$_{20}$O$_3$: C, 83.15; H, 4.98.

Dimethyl 2-chloro-2-(9-xanthenyl)malonate (3p): colorless needles (from EtOH); mp 138.8–139.7 °C; IR (CHCl$_3$) ν 1742 (C=O); ^{1}H NMR (CCl$_4$) δ 3.76 (6 H, s, 2 OMe), 5.35 (1 H, s, –CH<), 7.00–7.73 (8 H, m, arom, H). Anal. Found: C, 62.22; H, 4.41. Calcd for C$_{18}$H$_{15}$O$_5$Cl: C, 62.35; H, 4.36.

2-Phenyl-2-(9-xanthenyl)acetamide (3t). The cyano group of 2-phenyl-2-(9-xanthenyl)acetonitrile was hydrolyzed during the oxidation to give 2-phenyl-2-(9-xanthenyl)acetamide:[29] colorless needles (from EtOH); mp 197.8–198.5 °C; IR (CHCl$_3$) ν 3430 (NH$_2$), 1662 (C=O); ^{1}H NMR (CDCl$_3$) δ 3.57 (2 H, s, NH$_2$), 5.98 (1 H, br d, J = 9.0 Hz, –CH<), 6.41 (1 H, d, J = 9.0 Hz, –CH<), 6.92–7.46 (13 H, m, arom H). Anal. Found: C, 79.70; H, 5.53; N, 4.33. Calcd for C$_{21}$H$_{17}$O$_2$N: C, 79.98; H, 5.43; N, 4.44.

Reaction of 1a with [Mn(OAc)$_3$] in the Presence of Other Radical Sources. Bromomalonic acid (**2w**), diethyl phenylmalonate (**2x**), nitroethane, ethyl phenylacetate, 2,5-hexanedione, ethyl levulinate, and acetonitrile were also examined instead of **2a–v**. The reaction using **2w** gave a complex mixture, and a dimer (**6x**) only was isolated when **2x** was added to a similar reaction system. In the case of nitroethane, ethyl phenylacetate, 2,5-hexanedione, ethyl levulinate, and acetonitrile, the expected radical-trapped products were not obtained, but only 9-xanthenone was isolated after separation in 24%, 63%, 27%, 32%, and 45% yield, respectively.

Oxidation of 1a with [Mn(OAc)$_3$] in the Presence of Acetic Anhydride. A mixture of **1a** (1 mmol), acetic anhydride (4 mmol), and [Mn(OAc)$_3$] (4 mmol) was heated under reflux in glacial acetic acid (25 mL) until the brown color of Mn(III) disappeared (for 126 min). The solvent was removed in vacuo and the residue was treated with the same workup previously described to yield **5a** and a mixture of three isomers of (acetoxymethyl)-9-xanthenone (**8**).[8]

Oxidation of Thioxanthene (9) with [Mn(OAc)$_3$] in the Presence of β-Dicarbonyl Compounds (2a–c). A similar oxidation using **9** instead of **1a** was carried out in boiling acetic acid, and the same workup previously mentioned was conducted.

3-(9-Thioxanthenyl)-2,4-pentanedione (10a): colorless needles (from EtOH); mp 165–168 °C; IR (CHCl$_3$) ν 1728, 1695 (C=O); ^{1}H NMR (CDCl$_3$) δ 1.84 (6 H, s, 2 COMe), 4.85 (1 H, d, J = 11.0 Hz, –CH<), 5.08 (1 H, d, J = 11.0 Hz, –CH<), 7.20–7.66 (8 H, m, arom H). Anal. Found: C, 72.41; H, 5.34. Calcd for C$_{18}$H$_{16}$O$_2$S: C, 72.11; H, 5.38.

3-(9-Thioxanthenylidene)-2,4-pentanedione (11a): pale brown needles (from EtOH); mp 139–140 °C; IR (CHCl$_3$) ν 1711 (C=O); ^{1}H NMR (CDCl$_3$) δ 2.00 (6 H, s, 2 COMe), 7.23–7.67 (8 H, m, arom H). Anal. Found: C, 73.15; H, 5.00. Calcd for C$_{18}$H$_{14}$O$_2$S: C, 73.44; H, 4.79.

Reaction of Substituted Xanthenes (1b–e) with 2a or 2b in the Presence of [Mn(OAC)$_3$]. A substituted xanthene (1 mmol) and **2a** or **2b** (4 mmol) were dissolved in glacial acetic acid (30 mL), and [Mn(OAc)$_3$] (4 mmol) was added just before refluxing. The mixture was heated under reflux until the brown color of [Mn(OAc)$_3$] turned colorless. The solvent was removed in vacuo, and the same workup previously mentioned was done. The reaction times and the yields are summarized in Table II.

3-(3-Methoxy-9-xanthenyl)-2,4-pentanedione (3ab): pale yellow needles (from EtOH); mp 100–101 °C; IR (CHCl$_3$) ν 1733, 1699 (COMe); ^{1}H NMR (CDCl$_3$) δ 1.80 (3 H, s, COMe), 1.83 (3 H, s, COMe), 3.76 (3 H, s, OMe), 4.04 (1 H, d, J = 10.0 Hz, >CH–), 4.78 (1 H, d, J = 10.0 Hz, >CH–), 6.48–7.25 (7 H, m, arom H). Anal. Found: C, 73.55; H, 5.74. Calcd for C$_{19}$H$_{18}$O$_4$: C, 73.53; H, 5.85.

3-(3-Methoxy-9-xanthenylidene)-2,4-pentanedione (4ab): pale yellow microcrystals (from EtOH); mp 66–67 °C; IR (CHCl$_3$) ν 1708 (COMe); ^{1}H NMR (CDCl$_3$) δ 2.20 (6 H, s, 2 COMe), 3.86 (3 H, s, OMe), 6.63–7.49 (7 H, m, arom H). Anal. Found: C, 74.20; H, 5.02. Calcd for C$_{19}$H$_{16}$O$_4$: C, 74.01; H, 5.23.

3-(1-Methoxy-9-xanthenyl)-2,4-pentanedione (3ad):[30] colorless needles (from EtOH); mp 149–150 °C; IR (CHCl$_3$) ν 1696 (COMe); ^{1}H NMR (CDCl$_3$) (keto form) δ 1.78 (3 H, s, COMe), 2.05 (3 H, s, COMe), 3.76 (3 H, s, OMe), 3.91 (1 H, d, J = 6.0 Hz, >CH–), 5.12 (1 H, d, J = 6.0 Hz, >CH–), 6.38–7.58 (7 H, m, arom H); (enol form) 1.78 (3 H, s, COMe), 2.05 (3 H, s, COMe), 3.71 (3 H, s, OMe), 5.28 (1 H, s, >CH–), 6.38–7.58 (7 H, m, arom H), 17.31 (1 H, s, OH). Anal. Found: C, 73.37; H, 5.75. Calcd for C$_{19}$H$_{18}$O$_4$: C, 73.53; H, 5.85.

3-(1-Methoxy-9-xanthenylidene)-2,4-pentanedione (4ad): pale yellow needles (from EtOH); mp 108–109 °C; IR (CHCl$_3$) ν 1679 (COMe); ^{1}H NMR (CDCl$_3$) δ 2.10 (3 H, br s, COMe), 2.22 (3 H, br s, COMe), 3.77 (3 H, s, OMe), 6.60–7.45 (7 H, m, arom H). MS m/z (rel intensity), 308 (M$^+$, 11), 277 (100), 251 (8), 221 (6), 180 (5). Anal. Found: C, 73.72; H, 5.20. Calcd for C$_{19}$H$_{16}$O$_4$: C, 74.01; H, 5.23.

Effect of Additives for the Reaction of 1a with 2a or 2b in the Presence of [Mn(OAc)$_3$]. The compounds **1a** (1 mmol),

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(29) Sato, H.; Nishino, H.; Kurosawa, K. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 1753.

(30) The product **3ad** was obtained as a 3:1 mixture of keto and enol.

2a or **2b** (4 mmol), and the additive of which the amount used as shown in Table III were dissolved in glacial acetic acid (30 mL) while [Mn(OAc)$_3$] (4 mmol) was added just before refluxing. The mixture was heated under reflux for the period described in Table III. After workup, the products listed in Table III were isolated.

Reaction of Radical-Trapping Reagents with 2a in the Presence of [Mn(OAc)$_3$]. The reaction of fluorene (1 mmol) with **2a** (4 mmol) and [Mn(OAc)$_3$] (4 mmol) was carried out in boiling glacial acetic acid (30 mL) for 3 min (32% conversion) to afford 9-acetoxyfluorene (12%).[31] A mixture of 9,10-dihydroacridine (1 mmol) and **2a** (4 mmol) was oxidized with [Mn(OAc)$_3$] (4 mmol) for 1 min (100% conversion) to give only acridine (54%) which was identical to an authentic sample. A similar reaction of 9,10-dihydro-10-methylacridine (1 mmol) and **2a** (4 mmol) with [Mn(OAc)$_3$] (4 mmol) for 1 min (100% conversion) yielded a tarry material, and no radical-trapped products were isolated. 9,10-Dihydroanthracene (1 mmol) reacted with **2a** (4 mmol) in the presence of [Mn(OAc)$_3$] (4 mmol) for 1 min (75% conversion) to give 9-(1-acetyl-2-hydroxy-1-propenyl)anthracene (19%) and 9,10-bis(1-acetyl-2-hydroxy-1-propenyl)anthracene (9%).[12a] Acridine (1 mmol) was oxidized with [Mn(OAc)$_3$] (4 mmol) in the presence of **2a** (4 mmol) for 1 min (100% conversion), and only 9-(1-acetyl-2-hydroxy-1-propenyl)acridine (14%)[12a] was isolated along with a complex mixture. The reactions of dibenzosuberone (1 mmol), triptycene (1 mmol), and diphenylmethane (**13a**, 1 mmol) were run at the molar ratio of 1:4:4 for 5, 4, and 4 min (12% conversion), respectively, and only starting materials were recovered. The similar reactions of bis(4-methoxyphenyl)methane (**13b**, 1 mmol) and bis(2,4-dimethoxyphenyl)methane (**13c**, 1 mmol) at the molar ratio of 1:4:4 were conducted for 3 min (24% conversion) and 1 min (84% conversion), respectively, and **14b** (9%) and **14c** (42%) were obtained.

3-[Bis(2,4-dimethoxyphenyl)methyl]-2,4-pentanedione (14c): colorless microcrystals (from EtOH); mp 147–148 °C; IR (CHCl$_3$) ν 1693 (C=O); ^{1}H NMR (CDCl$_3$) δ 1.97 (6 H, s, 2 COMe), 3.70 (6 H, s, 2 OMe), 3.74 (6 H, s, 2 OMe), 5.00 (1 H, d, J = 12.6 Hz, >CH–), 5.27 (1 H, d, J = 12.6 Hz, >CH–), 6.23–7.34 (6 H, m, arom H). Anal. Found: C, 68.20; H, 6.80. Calcd for $C_{22}H_{26}O_6$: C, 68.38; H, 6.78.

The reaction of BHT (1 mmol) with **2a** (4 mmol) in the presence of [Mn(OAc)$_3$] (4 mmol) was performed for 1 min in boiling glacial acetic acid (30 mL) to yield **15** (32%) and **16** (5%). When water (800 mmol) was added to the same reaction mixture, the yield of **15** and **16** increased up to 65% and 6%, respectively.

4-(Diacetylmethyl)-2,6-di-*tert*-butyl-4-methyl-2,5-cyclohexadienone (15): colorless microcrystals (from hexane); mp 61–62 °C; IR (CHCl$_3$) ν 1694, 1658 (C=O); ^{1}H NMR (CDCl$_3$) δ 1.23 (18 H, s, 6 Me), 1.30 (3 H, s, Me), 2.13 (6 H, s, 2 Me), 3.96 (1 H, s, >CH—), 6.80 (2 H, s, =CH—). Anal. Found: C, 75.22; H, 9.50. Calcd for $C_{20}H_{30}O_3$: C, 75.43; H, 9.50.

4-(Diacetylmethylene)-2,6-di-*tert*-butyl-2,5-cyclohexadien-1-one (16):[20] orange prisms (from EtOH); mp 86–87 °C; IR (CHCl$_3$) ν 1680, 1626 (C=O); ^{1}H NMR (CDCl$_3$) δ 1.26 (18 H, s, 6 Me), 2.44 (6 H, s, 2 COMe), 7.13 (2 H, s, =CH—). Anal. Found: C, 75.21; H, 8.66. Calcd for $C_{19}H_{26}O_3$: C, 75.46; H, 8.67.

Reaction of 9-Hydroxyxanthene (17, R = H) with [Mn(OAc)$_3$]. A mixture of 9-hydroxyxanthene (103.2 mg) and [Mn(OAc)$_3$] (252.7 mg) was heated under reflux in glacial acetic acid (10 mL) for 120 min. The solvent was removed, and the residue was separated to give **5a** (74.4 mg, 73%) and **1a** (16.2 mg, 17%) after treatment in a manner analogous to that previously described.

Reaction of 9-Acetoxyxanthene (17, R = Ac) or 9-Hydroxyxanthene (17, R = H) with 2a or 2b in the Presence of Manganese(II) Acetate. A mixture of **17** (R = Ac) (60.4 mg), **2a** (51 μL), and manganese(II) acetate tetrahydrate, Mn(OAc)$_2$·4H$_2$O, (125.6 mg) was heated under reflux for 1 min in glacial acetic acid (2 mL). The solvent was removed, and the residue was treated with 2 M HCl (2 mL). The aqueous solution was extracted with CHCl$_3$ to give **3a** (65.3 mg, 93%). A similar reaction of **17** (R = H) (100.1 mg) with **2a** (110 μL) in the presence of Mn(OAc)$_2$·4H$_2$O (247.0 mg) was carried out in boiling glacial acetic acid (15 mL) for 30 min to give **3a** (125.5 mg, 89%). A similar reaction of **17** (R = H) (40.3 mg) with **2b** (46 μL) in the presence of Mn(OAc)$_2$·4H$_2$O (99.5 mg) in glacial acetic acid (1 mL) for 30 min gave **3b** (61.4 mg, 97%).

Competition Reaction of 2a in the Presence of 1a and BHT. A mixture of **1a** (0.5 mmol), BHT (0.5 mmol), and **2a** (4 mmol) was dissolved in hot glacial acetic acid (30 mL), and [Mn(OAc)$_3$] (4 mmol) was added. The mixture was heated under reflux for 1 min and then the solvent was removed in vacuo. The residue was treated by the method previously mentioned, and **3a** (27%), **4a** (33%), **15** (67%), and **16** (6%) were obtained after separation.

Registry No. **1a**, 92-83-1; **1b**, 30414-79-0; **1c**, 141247-89-4; **1d**, 100621-82-7; **1e**, 141247-90-7; **2a**, 123-54-6; **2b**, 108-59-8; **2c**, 105-53-3; **2d**, 108-13-4; **2e**, 120-46-7; **2f**, 18362-51-1; **2g**, 93-91-4; **2h**, 94-02-0; **2i**, 141-97-9; **2j**, 1830-54-2; **2k**, 105-50-0; **2l**, 109-77-3; **2m**, 107-91-5; **2n**, 105-56-6; **2o**, 141-82-2; **2p**, 28868-76-0; **2q**, 868-26-8; **2r**, 609-08-5; **2s**, 607-81-8; **2t**, 140-29-4; **2u**, 67-64-1; **2v**, 75-52-5; **2w**, 600-31-7; **2x**, 83-13-6; **3a**, 106917-00-4; **3b**, 13210-17-8; **3c**, 13210-18-9; **3d**, 134255-41-7; **3e**, 141221-66-1; **3f**, 141221-67-2; **3g**, 141221-68-3; **3h**, 141247-91-8; **3i**, 76461-98-8; **3j**, 141221-69-4; **3k**, 141221-70-7; **3l**, 6235-15-0; **3m**, 26004-40-0; **3n**, 26592-92-7; **3o**, 101278-43-7; **3p**, 141221-71-8; **3q**, 141221-72-9; **3r**, 141221-73-0; **3s**, 141221-74-1; **3t**, 141221-76-3; **3t′**, 141221-75-2; **3u**, 4819-85-6; **3ab**, 141221-77-4; **3ac**, 141221-78-5; **3ad**, 141221-79-6; **3ae**, 141221-80-9; **3bb**, 141221-81-0; **3bc**, 141221-82-1; **4a**, 55164-22-2; **4b′**, 141221-65-0; **4ab**, 141221-83-2; **4ac**, 141221-84-3; **4ad**, 141221-85-4; **4ae**, 141221-86-5; **4bc**, 141221-87-6; **5a**, 90-47-1; **5c**, 15007-07-5; **6f**, 141221-88-7; **7a**, 141221-89-8; **7b**, 141221-90-1; **7c**, 141221-91-2; 8, 141221-97-8; **9**, 261-31-4; **10a**, 141221-92-3; **10b**, 13210-19-0; **10c**, 13210-20-3; **11a**, 141221-93-4; **13b**, 726-18-1; **13c**, 72046-68-5; **14b**, 141221-94-5; **14c**, 141221-95-6; **15**, 141221-96-7; **16**, 139978-29-3; **17** (R = H), 90-46-0; **17** (R = Ac), 35598-76-6; BHT, 128-37-0.

Supplementary Material Available: ^{1}H, ^{13}C NMR, IR, and MS spectral data, melting points, and elemental analyses data of oxidation products **3a,c,d,f–o,q–s,u,v**, **4a–c**, **4b′**, **5a**, **6f,x**, **7b,c**, **10b,c**, **14b**, **3ac**, **3ae**, **3bb**, **3bc**, **4ac**, **4ae**, **4bb**, and **4bc**, materials, supplementary references, and Table IV (9 pages). Ordering information is given on any current masthead page.

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(31) Bunton, C. A.; Israel, G.; Mhala, M. M. Williams, D. L. H. *J. Chem. Soc.* **1958**, 3718.