A New Synthesis of 9-Xanthenones by the Reaction of 2-Hydroxybenzophenones with Metal Salts

Shuichi UEDA* and Kazu KUROSAWA

Department of Chemistry, Faculty of Science, Kumamoto University, Kurokami-2-39-1, Kumamoto 860

(Received June 10, 1976)

Seven 2-hydroxy-4-methoxybenzophenones were oxidized with manganese(III) acetate to give 9-xanthenones (24—65%). 2-Hydroxy-3',4,4',6-tetramethoxybenzophenone gave 1,3,6,7-tetramethoxy-9-xanthenone in a 5% yield. 2-Hydroxy-3',4,4',5-tetramethoxybenzophenone yielded 2,5-dihydroxy-3',4,4'-trimethoxybenzophenone (9%). The oxidation of the 2-hydroxybenzophenones with lead tetraacetate also gave the 9-xanthenones, but in poor yields.

In a previous paper,[1] it has been reported that the reactions of 2-hydroxy-4-methoxy- and 2-hydroxy-4,4'-dimethoxybenzophenones with metal salts gave rise to dimeric compounds and 2,5-dihydroxybenzophenones. It was also reported that 2-hydroxy-2',4,4'-trimethoxy- and 2-hydroxy-3',4,4'-trimethoxybenzophenones yielded 3,6-dimethoxy- and 2,3,6-trimethoxy-9-xanthenones respectively. We have now continued our investigation of the reaction in the hope that this can lead to a new synthesis of 9-xanthenones.

The 2-hydroxybenzophenones were prepared by the known method,[2] while the reactions of the 2-hydroxybenzophenones with manganese(III) acetate and lead tetraacetate were carried out in boiling acetic acid. The structures of the reaction products were determined by examining their IR, NMR, and mass spectra, and by elemental analyses.

When 2-hydroxy-2',4,5'-trimethoxybenzophenone (Ie) was oxidized with manganese(III) acetate, 2,6-dimethoxy-9-xanthenone (IIb) (65%) was obtained. This indicates that an intramolecular coupling between the hydroxyl group and the carbon (2') in Ie took place and that the 2'-methoxyl group on that position was removed.

When Ie was oxidized with lead tetraacetate, 2,6-dimethoxy-1-methyl-9-xanthenone (IIe) (3%) and 1-acetoxymethyl-2,6-dimethoxy-9-xanthenone (IIIe) (6%) were obtained, together with IIb (11%). The NMR spectrum of IIe in CF_3COOH showed the presence of a methyl group {δ 2.96 (s, 3H)}, two methoxyl groups {δ 4.10 (s, 3H) and δ 4.15 (s, 3H)}, three aromatic protons {δ 7.24 (d, J=2 Hz), δ 7.34 (dd, J=9, 2 Hz) and δ 8.45 (d, J=9 Hz)}, and two aromatic protons {δ 7.78 (d) and 7.99 (d), AB system, J=9 Hz}. The methyl group at δ 2.96 can be located at the 1-position on the basis of its extraordinary lower shift[3] and on the basis of the presence of the lower-field doublet at δ 8.45 (J=9 Hz) as a result of the hydrogen adjacent to the carbonyl group. The presence of the aromatic AB system (J=9 Hz) further confirmd the IIe structure. A similar methylation of aromatic compounds and the acetoxylation of an aromatic methyl group have been reported in the reaction of lead tetraacetate.[4] The oxidation of 2-hydroxy-2',4-dimethoxybenzophenone (Ia) and 2-hydroxy-2',4,4'-trimethoxybenzophenone (Ic), both with a 2'-methoxyl group, gave 3-methoxy-9-xanthenone (IIa) (49% with $Mn(OAc)_3$ and 16% with $Pb(OAc)_4$) and 3,6-dimethoxy-9-xanthenone (IIc) (45% with $Mn(OAc)_3$ and 12% with $Pb(OAc)_4$, with the loss of the 2'-methoxyl group, respectively. In the oxidation of Ic with manganese(III) acetate, IV (9%) was isolated; however, its structure could not be determined.

When 2-hydroxy-3',4,4',5'-tetramethoxybenzophenone (If) was subjected to oxidation with manganese(III) acetate, 2,3,4,6-tetramethoxy-9-xanthenone (IIf) was obtained in a 48% yield, whereas the oxidation of If with lead tetraacetate afforded IIf in only a 7% yield, plus 1-acetoxymethyl-2,3,4,6-tetramethoxy-9-xanthenone (IIIf) (6%). 2-Hydroxy-3',4-dimethoxybenzophenone (Ib) and 2-hydroxy-3',4,4'-trimethoxybenzophenone (Id) gave IIb (24%) and 2,3,6-trimethoxy-9-xanthenone (IId) (40%) respectively, showing that the coupling occurred preferentially at the less hindered position.

When 2,4'-dihydroxy-3',4,5'-trimethoxybenzophenone (Ig) was oxidized with manganese (III) acetate, 2,6-dimethoxy-*p*-benzoquinone (V) (13%) was the only isolable product. There were many unidentified compounds in the reaction mixture, suggesting that the oxidation of dihydroxybenzophenones is not useful for the synthesis of 9-xanthenone. A monoacetate of Ig, 2-hydroxy-4'-acetoxy-3',4,5'-trimethoxybenzophenone (Ih), did, however, give 3-acetoxy-2,4,6-trimethoxy-9-xanthenone (IIh) (31%). This may indicate that hydroxy-9-xanthenones can be prepared from dihydroxybenzophenones *via* their acetate.

The manganese (III) acetate oxidation of 2-hydroxy-3',4,4',6-tetramethoxybenzophenone (Ii), which possesses a phloroglucinol nucleus, yielded 1,3,6,7-tetramethoxy-9-xanthenone (IIi) (5%) and 2,6-dimethoxy-3-(3,4-dimethoxybenzoyl)-*p*-benzoquinone (VIi) (5%). The lead tetraacetate oxidation of Ii afforded IIi in a better yield (11%), plus VIi (7%) and 2,6-dimethoxy-3-(3,4-dimethoxybenzoyl)-5-methyl-*p*-benzoquinone(VIi') (7%). A similar methylation is often observed in the reaction of a quinone with lead tetraacetate.[4]

Finally, we examined the oxidation of 2-hydroxy-3',4,4',5-tetramethoxybenzophenone (Ij). 2,5-Dihydroxy-3',4,4'-trimethoxybenzophenone (Ik) (9%) was obtained, together with many unidentified products.

Although 9-xanthenones have been synthesized in a number of ways, *i.e.*, by the dehydration of 2,2'-dihydroxybenzophenones,[2] the base-catalysed cyclization of 2-hydroxy-2'-methoxybenzophenones,[5] the cyclization of *o*-phenoxybenzoic acids,[6] and the oxidative couplings

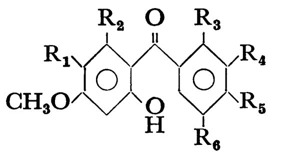
---

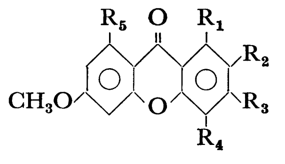
* Present address: Tokushima Factory, Taiho Co., Ltd., Hiraishi, Kawauchi-machi, Tokushima 771-01.

TABLE 1. THE REACTION OF 2-HYDROXYBENZOPHENONES WITH MANGANESE(III) ACETATE AND LEAD TETRAACETATE IN BOILING ACETIC ACID

Substrate	Reaction conditions			Products (yield, %)				
	Reagent	Molar ratio	Time (min)	9-Xanthenone	Acetoxymethyl-9-xanthenone	Quinone	Benzophenone	*etc.*
Ia	$Mn(OAc)_3$	1:4	180	IIa[10] (49)				
Ia	$Pb(OAc)_4$	1:3	120	IIa (16)				
Ib	$Mn(OAc)_3$	1:4	120	IIb[11] (24)				
Ic[1]	$Mn(OAc)_3$	1:4	180	IIc[1] (45)				IV(9)
Ic	$Pb(OAc)_4$	1:3	120	IIc (12)				
Id[1]	$Mn(OAc)_3$	1:4	90	IId[1] (40)				
Ie	$Mn(OAc)_3$	1:5	180	IIb (65)				
Ie	$Pb(OAc)_4$	1:3	150	IIb (11), IIe(3)	IIIe(6)			
If	$Mn(OAc)_3$	1:5	240	IIf (48)				
If	$Pb(OAc)_4$	1:3	120	IIf (7)	IIIf(6)			
Ig	$Mn(OAc)_3$	1:5	240			V (13)		
Ih	$Mn(OAc)_3$	1:4	120	IIh (31)				
Ii	$Mn(OAc)_3$	1:5	60	IIi (5)		VIi (5)		
Ii	$Pb(OAc)_4$	1:3	100	IIi[12] (11)		VIi (7), VIi′(7)		
Ij[9]	$Mn(OAc)_3$	1:4	120				Ik(9)	

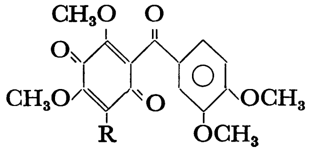
of polyhydroxybenzophenones with potassium permanganate,[6] potassium ferricyanide[7] and dichlorodicyano-*p*-benzoquinone,[8] it is now demonstrated that 9-xanthenones can be synthesized from 2-hydroxy-4-methoxy- and 2-hydroxy-4,6-dimethoxybenzophenones in moderate yields, by the reaction of manganese(III) acetate, but not from 2-hydroxy-4,5-dimethoxybenzophenone. Acetoxy-9-xanthenones, which could not be obtained by the previous methods, can also be prepared by the oxidation of 2-hydroxyacetoxybenzophenones.



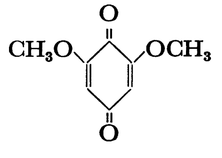


Ia $R_1=R_2=R_4=R_5=R_6=H$, $R_3=OCH_3$
Ib $R_1=R_2=R_3=R_5=R_6=H$, $R_4=OCH_3$
Ic $R_1=R_2=R_4=R_6=H$, $R_3=R_5=OCH_3$
Id $R_1=R_2=R_3=R_6=H$, $R_4=R_5=OCH_3$
Ie $R_1=R_2=R_4=R_5=H$, $R_3=R_6=OCH_3$
If $R_1=R_2=R_3=H$, $R_4=R_5=R_6=OCH_3$
Ig $R_1=R_2=R_3=H$, $R_4=R_6=OCH_3$, $R_5=OH$
Ih $R_1=R_2=R_3=H$, $R_4=R_6=OCH_3$, $R_5=OAc$
Ii $R_1=R_3=R_6=H$, $R_2=R_4=R_5=OCH_3$
Ij $R_2=R_3=R_6=H$, $R_1=R_4=R_5=OCH_3$
Ik $R_2=R_3=R_6=H$, $R_1=OH$, $R_4=R_5=OCH_3$

IIa $R_1=R_2=R_3=R_4=R_5=H$
IIb $R_1=R_3=R_4=R_5=H$, $R_2=OCH_3$
IIc $R_1=R_2=R_4=R_5=H$, $R_3=OCH_3$
IId $R_1=R_4=R_5=H$, $R_2=R_3=OCH_3$
IIe $R_3=R_4=R_5=H$, $R_1=CH_3$, $R_2=OCH_3$
IIf $R_1=R_5=H$, $R_2=R_3=R_4=OCH_3$
IIh $R_1=R_5=H$, $R_2=R_4=OCH_3$, $R_3=OAc$
IIi $R_1=R_4=H$, $R_2=R_3=R_5=OCH_3$
IIIe $R_3=R_4=R_5=H$, $R_1=CH_2OAc$, $R_2=OCH_3$
IIIf $R_2=R_3=R_4=OCH_3$, $R_1=CH_2OAc$, $R_5=H$



VIi R=H
VIi′ $R=CH_3$



V

Experimental

All the ${}^1H$ NMR spectra were recorded for the deuteriochloroform solution, unless otherwise stated, with a Hitachi R 24 NMR spectrometer, with tetramethylsilane as the internal reference. The IR spectra were recorded for the chloroform solution with a JASCO IRA-1 grating spectrometer, while the UV spectra were measured for the methanol solution with a Hitachi EPS-3T spectrophotometer. The mass spectrum was recorded with a Hitachi RMU-6M spectrometer. The melting points were determined with a Yanagimoto hot-stage apparatus and were uncorrected.

Preparations of 2-Hydroxybenzophenones (Ia,Ib,Ie—Ii). The 2-hydroxybenzophenones (Ia Ib, Ie, and Ig) were prepared by the reaction of 3-methoxyphenol (8 mmol) and a benzoic acid (8 mmol) with phosphoryl chloride (7 ml) containing fused zinc chloride (3 g), with heating at 65—70 °C for 2 h. The reaction mixture was poured into water and extracted with chloroform. After the removal of the chloroform, the crude 2-hydroxybenzophenone was purified on a silica gel column (Wakogel C 100) (100 g), eluting with benzene, followed by recrystallization from methanol.

2-Hydroxy-2′,4-dimethoxybenzophenone (Ia): Mp 88.5—89 °C, 68%, ν_{max}: 1630 cm^{-1} (C=O), λ_{max} (ε): 286 (14400) and 325 nm (9550), δ: 3.75 (s, OCH_3), 3.81 (s, OCH_3), 6.15—6.5 (m, 2H), 6.8—7.6 (m, 5H), and 12.6 (s, OH). Found: C, 69.68; H, 5.37%. Calcd for $C_{15}H_{14}O_4$: C, 69.75; H, 5.46%.

2-Hydroxy-3′,4-dimethoxybenzophenone (Ib): $Bp_{0.3}$ 165—170 °C (bath temp), 54%, ν_{max}: 1630 cm^{-1} (C=O), λ_{max} (ε): 292 (8970) and 325 nm (6780), δ: 3.81 (s, $2\times OCH_3$), 6.2—6.5 (m, 2H), 6.9—7.6 (m, 5H) and 12.4 (s, OH). Found: C, 69.55; H, 5.47%. Calcd for $C_{15}H_{14}O_4$: C, 69.75; H, 5.46%.

2-Hydroxy-2′,4,5′-trimethoxybenzophenone (Ie): Mp 110 °C, 21%, ν_{max}: 1628 cm^{-1} (C=O), λ_{max} (ε): 230 (s) (12300), 287 (15000) and 327 nm (9700), δ: 3.66 (s, OCH_3), 3.72 (s, OCH_3), 3.79 (s, OCH_3), 6.2—6.5 (m, 2H), 6.7—7.3 (m, 4H) and 12.5 (broad s, OH). Found: C, 66.65; H, 5.57%. Calcd for $C_{16}H_{16}O_5$: C, 66.66; H, 5.59%.

2,4′-Dihydroxy-3′,4,5′-trimethoxybenzophenone (Ig): Ig was prepared by the reaction of 3-methoxyphenol (8 mmol) and

3,4,5-trimethoxybenzoic acid (8 mmol) · with phosphoryl chloride (7 ml) containing fused zinc chloride (3 g); mp 142—143 °C, 32%, ν_{max}: 1620 cm^{-1} (C=O), λ_{max} (ε): 241 (s) (10900), 920 (11400) and 344 nm (14600), δ: 3.79 (s, OCH_3), 3.84 (s, 2×OCH_3), 6.0 (broad s, OH), 6.2—6.45 (m, $H_{(3)}$ and $H_{(5)}$), 6.84 (s, $H_{(2')}$ and $H_{(6')}$), 7.45 (d, J=8.5 Hz, $H_{(6)}$) and 12.5 (broad s, OH). Found: C, 63.24; H, 5.36%. Calcd for $C_{16}H_{16}O_6$: C, 63.15; H, 5.30%.

2-Hydroxy-3′,4,4′,5′-tetramethoxybenzophenone (If): A mixture of Ig (6 g), dimethyl sulfate (3 ml), potassium carbonate (5 g), and acetone (50 ml) was heated under reflux for 30 min. After the removal of the acetone, the resulting mixture was extracted with benzene. The benzene was evaporated *in vacuo*, and the resulting liquid was allowed to crystallize from methanol to give If (3.6 g, 57%); mp 106—107 °C, ν_{max}: 1630 cm^{-1} (C=O), λ_{max} (ε): 293 (16300) and 328 nm (15200), δ: 3.81 (s, OCH_3), 3.84 (s, 2×OCH_3), 3.88 (s, OCH_3), 6.25—6.55 (m, $H_{(3)}$ and $H_{(5)}$), 6.83 (s, $H_{(2')}$ and $H_{(6')}$), 7.50 (d, J=8.5 Hz, $H_{(6)}$) and 12.50 (s, OH). Found: C, 64.11; H, 5.77%. Calcd for $C_{17}H_{18}O_6$: C, 64.14; H, 5.74%.

2-Hydroxy-4′-acetoxy-3′,4,5′-trimethoxybenzophenone (Ih): A mixture of Ig (1.30 g), acetic anhydride (480 mg), and pyridine (8 ml) was kept at room temperature for 24 h. The reaction mixture was then poured into water, and the resulting precipitates were collected and recrystallized from ethanol to give Ih (1.18 g, 80%); mp 124—125 °C, ν_{max}: 1630 (C=O) and 1770 cm^{-1} (OAc), λ_{max} (ε): 294 (13500) and 325 nm (11100), δ: 2.37 (s, OAc), 3.88 (s, 3×OCH_3), 6.3—6.8 (m, $H_{(3)}$ and $H_{(5)}$), 6.93 (s, $H_{(2')}$ and $H_{(6')}$), 7.65 (d, J=8.5 Hz, $H_{(6)}$) and 12.40 (s, OH). Found: C, 62.24; H, 5.51%. Calcd for $C_{18}H_{18}O_7$: C, 62.42; H, 5.24%.

2-Hydroxy-3′,4,4′,6-tetramethoxybenzophenone (Ii): A mixture of 3,5-dimethoxyphenol (4 g), 3,4-dimethoxybenzoyl chloride (5.5 g), aluminium chloride (12 g), and ether (50 ml) was stirred at room temperature for 48 h. By working up in a similar manner to the above, Ii (4.0 g, 49%) was obtained; mp 134 °C, ν_{max}: 1625 cm^{-1} (C=O), λ_{max} (ε): 233 (21900), 286 (11900) and 313 nm (12600), δ: 3.55 (s, OCH_3), 3.86 (s, OCH_3), 3.90 (s, OCH_3), 3.95 (s, OCH_3), 5.99 (d, 1H) and 6.19 (d, 1H) (AB system, J_{AB}=2.0 Hz), 6.19 (d, J=8.5 Hz, $H_{(5')}$), 6.75—6.90 (m, $H_{(2')}$ and $H_{(6')}$), and 11.60 (s, OH). Found: C, 64.22; H, 5.75%. Calcd for $C_{17}H_{18}O_6$: C, 64.14; H, 5.70%.

Oxidation of 2-Hydroxybenzophenones (Ia—Ii) with Manganese (III) Acetate. A mixture of 2-hydroxybenzophenone (1 mmol), manganese(III) acetate dihydrate[13] (4 or 5 mmol), and acetic acid (30 ml) was heated under reflux for the period of time shown in the Table. After the removal of the acetic acid *in vacuo*, the resulting solid was triturated with water and extracted with chloroform. The chloroform was removed *in vacuo* and the resulting products were purified on TLC (Wakogel B 10) and by recrystallization.

Ia gave 3-methoxy-9-xanthenone (IIa); mp 125—126 °C (EtOH) (lit,[10] mp 128—129 °C), 49%, ν_{max}: 1660 cm^{-1} (C=O), λ_{max} (ε): 239 (44100), 270 (12000) and 303 nm (17300), δ: 3.85 (s, OCH_3), 6.7—7.0 (m, 2H), 7.1—7.85 (m, 3H) and 8.1—8.45 (m, 2H).

Ib yielded 2,6-dimethoxy-9-xanthenone (IIb); mp 162 °C (EtOH) (lit,[11] mp 163.5—164.5 °C), 24%, ν_{max}: 1650 cm^{-1} (C=O), λ_{max} (ε): 243 (36500) and 312 nm (15700), δ: 3.88 (s, 2×OCH_3), 6.7—7.0 (m, $H_{(5)}$ and $H_{(7)}$), 7.0—7.5 (m, $H_{(3)}$ and $H_{(4)}$), 7.63 (d, J=2 Hz, $H_{(1)}$) and 8.20 (d, J=8 Hz, $H_{(8)}$).

Ic gave 3,6-dimethoxy-9-xanthenone (IIc) [mp 185 °C (EtOH) (lit,[1] mp 182—183 °C), 45%) and IV (mp 157 °C (benzene), 9%, ν_{max}: 1650, 1698 and 1758 cm^{-1}, λ_{max} (ε): 229 (24500), 267 (17400) and 290 nm (9670), δ: 3,75 (s, OCH_3), 3.82 (s, OCH_3), 5.50 (d, J=2 Hz, 1H), 6.16 (dd, J=10, 2 Hz, 1H), 6.40 (d, J=2 Hz, 1H), 6.64 (dd, J=8.2 Hz, 1H), 6.80 (d, J=10 Hz, 1H) and 7.81 (d, J=8 Hz, 1H). *m/e*: 288 (M^+), 150, 122 and 107. Found: C, 62.45; H, 4.21%. Calcd for $C_{15}H_{12}O_6$: C, 62.50; H, 4.20%].

Id yielded 2,3,6-trimethoxy-9-xanthenone (IId); mp 216—217 °C (EtOH) (lit,[1] mp 216—217 °C), 40%.

Ie gave IIb; mp 162 °C, 65%.

If yielded 2,3,4,6-tetramethoxy-9-xanthenone (IIf); mp 130 °C (EtOH), 48%, ν_{max}: 1655 cm^{-1} (C=O), λ_{max} (ε): 246 (38600), 272 (14000) and 313 (21100), δ: 3.92 (s, 2×OCH_3), 4.00 (s, OCH_3), 4.02 (s, OCH_3), 6.75—7.05 (m, $H_{(5)}$ and $H_{(7)}$), 7.46 (s, $H_{(1)}$) and 8.14 (d, J=8.5 Hz, $H_{(8)}$). Found: C, 64.35; H, 5.02%. Calcd for $C_{17}H_{16}O_6$: C, 64.55; H, 5.10%.

Ig yielded 2,6-dimethoxy-*p*-benzoquinone (V); mp 255 °C (EtOH) lit,[14] mp 255—256 °C), 12%, ν_{max}: 1660 and 1720 cm^{-1}, δ: 3.82 (s, 2×OCH_3) and 5.87 (s, $H_{(3)}$ and $H_{(5)}$).

Ih gave 3-acetoxy-2,4,6-trimethoxy-9-xanthenone (IIh); mp 166—167 °C (EtOH), 31%, ν_{max}: 1660 (C=O) and 1772 cm^{-1} (OAc), λ_{max} (ε): 247 (34000), 274 (12900) and 312 nm (16100), δ: 2.43 (s, OAc), 3.93 (s, 2×OCH_3), 4.08 (s, OCH_3), 6.9—7.1 (m, $H_{(5)}$ and $H_{(7)}$), 7.57 (s, $H_{(1)}$) 8.22 (d, J=8.5 Hz, $H_{(8)}$). Found: C, 62.74; H, 4.59%. Calcd for $C_{18}H_{16}O_7$: C, 62.79; H, 4.68%.

Ii yielded 1,3,6,7-tetramethoxy-9-xanthenone (IIi) (mp 202 °C (benzene) (lit,[12] mp 185—190 °C), 5%, ν_{max}: 1650 cm^{-1} (C=O), λ_{max} (ε): 256 (33100), 270 (s) (7100), 305 (11300) and 351 nm (9000), δ: 3.86 (s, OCH_3), 3.94 (s, 3×OCH_3), 6.30 (d, 1H) and 6.42 (d, 1H) (AB system, J=2 Hz, $H_{(2)}$ and $H_{(4)}$), 6.76 (s, $H_{(5)}$), and 7.62 (s, $H_{(8)}$)], and 2,6-dimethoxy-3-(3,4-dimethoxybenzoyl)-*p*-benzoquinone (VIi) [mp 161 °C (benzene), 5%, ν_{max}: 1655, 1688 and 1718 cm^{-1}, λ_{max} (ε): 236 (17600) and 289 nm (16200), δ: 3.85 (s, 2×OCH_3), 3.95 (s, 2×OCH_3), 5.90 (s, $H_{(5)}$), 6.85 (d, J=8.5Hz, $H_{(5')}$), 7.38 (dd, J=8.5, 2 Hz, $H_{(6')}$) and 7.55 (d, J=2 Hz, $H_{(2')}$). Found: C, 61.15; H, 4.89%. Calcd for $C_{17}H_{16}O_7$: C, 61.44; H, 4.85%].

Ij gave 2,5-dihydroxy-3′,4,4′-trimethoxybenzophenone (Ik); mp 208—209 °C (EtOH), 9%, ν_{max}: 1630 cm^{-1} (C=O), λ_{max} (ε): 239 (14800), 253 (14600), 287 (10600), and 372 nm (9850), δ: 3.95 (s, OCH_3), 3.97 (s, 2×OCH_3), 5.24 (s, OH), 6.58 (s, $H_{(3)}$), 6.95 (d, J=8.5 Hz, $H_{(5')}$), 7.23 (s, $H_{(6)}$), 7.2—7.45 (m, $H_{(2')}$ and $H_{(6')}$) and 12.30 (s, OH). Found: C, C, 63.06; H, 5.30%. Calcd for $C_{16}H_{16}O_6$: C, 63.15; H, 5.30 %.

Oxidation of 2-Hydroxybenzophenones (Ia, Ic, Ie, If, and Ii) with Lead Tetraacetate. A mixture of a 2-hydroxybenzophenone (5 mmol), lead tetraacetate[15] (15 mmol), and acetic acid (30 ml) was heated under reflux for the period of time shown in the Table. After the removal of the acetic acid *in vacuo*, the resulting products were triturated with 2M-hydrochloric acid and then extracted with chloroform. The chloroform solution was washed with aqueous sodium hydrogencarbonate, and the chloroform was evaporated again *in vacuo* to give crude products which were purified on TLC (Wakogel B 10) and by recrystallization. Ia gave IIa; mp 125—126 °C (EtOH), 16%. Ic yielded IIc; mp 185 °C (EtOH), 12%. Ie gave IIb (mp 162 °C (EtOH), 11%), 2,6-dimethoxy-1-methyl-9-xanthenone (IIe) [mp 173 °C (EtOH), 3%, ν_{max}: 1655 cm^{-1} (C=O), λ_{max} (ε): 244 (34300), 273 (s) (12200), 309 (13300), and 355 nm (4600), Found: C, 70.92; H, 5.25%. Calcd for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22%], and 1-acetoxymethyl-2,6-dimethoxy-9-xanthenone (IIIe) [mp 196 °C (benzene–light petroleum), 6%, ν_{max}: 1660 (C=O) and 1745 cm^{-1} (OAc), λ_{max} (ε): 242 (38200), 271 (s) (8900), 314 (14200) and 359 nm (5700), δ: 2.05 (s, OAc), 3.87 (s, 2×OCH_3), 5.85 (s, 2H, $-CH_2-$), 6.75 (d, J=2 Hz, $H_{(5)}$), 6.85 (dd, J=8.5, 2 Hz, $H_{(7)}$), 7.30 (d, 1H) and 7.43 (d, 1H) (AB system, J_{AB}=

8 Hz, $H_{(3)}$ and $H_{(4)}$), and 8.12 (d, J=8.5 Hz, $H_{(8)}$). Found: C, 65.88; H, 4.93%. Calcd for $C_{18}H_{16}O_6$: C, 65.85; H, 5.19%]. If gave IIf [mp 130 °C (EtOH), 7%] and 1-acetoxymethyl-2,3,4,6-tetramethoxy-9-xanthenone (IIIf) [mp 120—121 °C (benzene), 6%, ν_{max}: 1660 (C=O) and 1745 cm^{-1} (OAc), λ_{max} (ε): 248 (36500), 275 (10200), and 311 nm (17500), δ: 2.05 (s, OAc), 3.86 (s, 2×OCH_3), 4.03 (s, OCH_3), 4.06 (s, OCH_3), 5.72 (s, $-CH_2-$), 6.80 (d, J=2 Hz, $H_{(5)}$), 6.80 (dd, J=8.5, 2 Hz, $H_{(7)}$) and 8.00 (d, J=8.5 Hz, $H_{(8)}$). Found: C, 61.58; H, 5.21%. Calcd for $C_{20}H_{20}O_8$: C, 61.85; H, 5.19%]. Ii yielded IIi (mp 202 °C (benzene), 11%), VIi (mp 161 °C (benzene), 7%), and 2,6-dimethoxy-3-(3,4-dimethoxybenzoyl)-5-methyl-*p*-benzoquinone (VIi′) [mp 118—120 °C (benzene), 7% ν_{max}: 1650 and 1690 cm^{-1}, λ_{max} (ε): 236 (17800) and 288 nm (19000), δ: 1.95 (s, CH_3), 3.82 (s, OCH_3), 3.94 (s, 2×OCH_3), 4.01 (s, OCH_3), 6.86 (d, J=8.5 Hz, $H_{(5')}$), 7.35 (dd, J=8.5, 2 Hz, $H_{(6')}$) and 7.65 (d, J=2 Hz, $H_{(2')}$). Found: C, 62.44; H, 5.34%. Calcd for $C_{18}H_{18}O_7$: C, 62.42; H, 5.24%].

References

1) K. Kurosawa, Y. Sasaki, and M. Ikeda, *Bull. Chem. Soc. Jpn.*, **46**, 1498 (1973).

2) P. K. Grover, G. D. Shah, and R. C. Shah, *J. Chem. Soc.*, **1955**, 3982.

3) K. K. Chexal, J. S. E. Holker, T. J. Simpson, and K. Young, *J. Chem. Soc., Perkin Trans. 1*, **1975**, 543.

4) R. Criegee, "Oxidation in Organic Chemistry," Part A, ed by K. S. Wiberg, Academic Press, New York and London (1965), p. 277.

5) G. H. Stout and W. J. Balkenhol, *Tetrahedron*, **25**, 1949 (1969).

6) J. W. A. Findlay, P. Gupta, and J. R. Lewis, *J. Chem. Soc., C*, **1969**, 2761.

7) J. R. Lewis and B. H. Warrington *J. Chem. Soc.*, **1964**, 5074.

8) J. W. A. Findlay, P. Gupta, and J. R. Lewis, *J. Chem. Soc., D*, **1969**, 207.

9) B. J. Donnelly, D. M. X. Donnelly, and A. M. O'Sullivan, *Tetrahedron*, **24**, 2617 (1968).

10) *Chem. Abstr.*, **63**, 1484b (1965).

11) P. D. McDonald and G. A. Hamilton, *J. Am. Chem. Soc.*, **95**, 7752 (1973).

12) H. D. Locksley and J. G. Murray, *Phytochemistry*, **10**, 3179 (1971).

13) P. J. Andrulis, Jr., M. J. S. Dewar, R. Dietz, and R. L. Hunt, *J. Am. Chem. Soc.*, **88**, 5473 (1966).

14) F. Wessely and J. Koltan, *Monatsh. Chem.*, **84**, 291 (1953).

15) L. F. Audrieth, "Inorganic Syntheses," Vol. 3, McGraw-Hill, New York (1950), p. 47.