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Reactions of 1,8-Dimethoxy-9-phenylxanthen-9-ol in the Presence of an Acid, and Its Basicity

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In the presence of a catalytic amount of acid, the title xanthenol (**1**) reacted in acetone to give 1,8-dimethoxy-9-phenylxanthen-9-ylmethyl methyl ketone. Analogous reactions were observed for ethyl methyl ketone and acetophenone, but not for diethyl ketone. Propanal and butanal also reacted to give 2-(1,8-dimethoxy-9-phenylxanthen-9-yl)propanal and 2-(1,8-dimethoxy-9-phenylxanthen-9-yl)butanal, respectively. In hot primary and secondary alcohols, **1** was reduced to give 1,8-dimethoxy-9-phenylxanthene. **1** also reacted with methoxybenzenes, phenol, and *N*-alkylanilines to give 9-aryl-1,8-dimethoxy-9-phenylxanthenes. The basicity of **1**, or the stability of the carbenium ion ($pK_{R^+} = -0.81$), was measured in hydrochloric acid and compared with those of related 9-arylxanthen-9-ols, such as 1,8-dimethoxy-9-(2,6-dimethoxyphenyl)xanthen-9-ol (1.14), 9-(2,6-dimethoxyphenyl)xanthen-9-ol (4.80) (**8**), and 9-phenylxanthen-9-ol (0.75). The drastic differences in the reactivities and the basicity between **1** and **8** were attributed to a steric effect rather than an electronic effect.

The chemical properties of di- and triphenylmethanols vary drastically depending on the number and position of the methoxy substituent on the phenyl groups.[1—5] Thus, bis(2,4,6-trimethoxyphenyl)carbenium salt, $[\Phi^a_2CH]ClO_4$ $[\Phi^a = 2,4,6\text{-}(MeO)_3C_6H_2]$, is recrystallizable even from methanol,[4] and arylbis(2,6-dimethoxyphenyl)carbenium salts, $[Ar\Phi^b_2C]ClO_4$ $[\Phi^b = 2,6\text{-}(MeO)_2C_6H_3]$, show a variety of unusual reactivities, depending on the Ar group.[1,2] These carbenium salts decompose in water to give the xanthene derivatives[1] or result in Φ–C bond cleavage.[4] 1,8-Dimethoxy-9-phenylxanthen-9-ol (**1**) was obtained by the decomposition of bis(2,6-dimethoxyphenyl)phenyl-methanol, $Ph\Phi^b{}_2COH$, in hot acidic water.[1] For further understanding the effect of *ortho*-methoxy substitutions, we were also interested in the properties of **1** in common organic solvents in the presence of an acid. We report here on its facile reactions to give compounds **2**—**6** in Scheme 1. The reactivities, as well as the basicity, were compared with those of the related compounds (**7**—**9**) in Scheme 2 with a hope to elucidate the steric and/or the electronic effects of *ortho*-methoxy substituents.

Experimental

General. 1,8-Dimethoxy-9-phenylxanthen-9-ol (**1**) was prepared as described elsewhere;[1] MS: *m*/*z* (%) 334 (M^+; 2), 257 ($[M-Ph]^+$; 100).

The NMR spectra were recorded for solutions in $CDCl_3$ using a JEOL model JNM-GX-270 spectrometer. IR spectra were recorded for Nujol® mulls using a Shimadzu FTIR-4200 spectrophotometer. GC-MS spectra were recorded for acetone solutions using a Shimadzu QP-5000 mass spectrometer (gasified at 250 °C). UV-vis spectra were recorded using a Shimadzu UV-160 spectrophotometer. The ^1H and ^{13}C NMR spectral data are summarized in Tables 1 and 2, respectively.

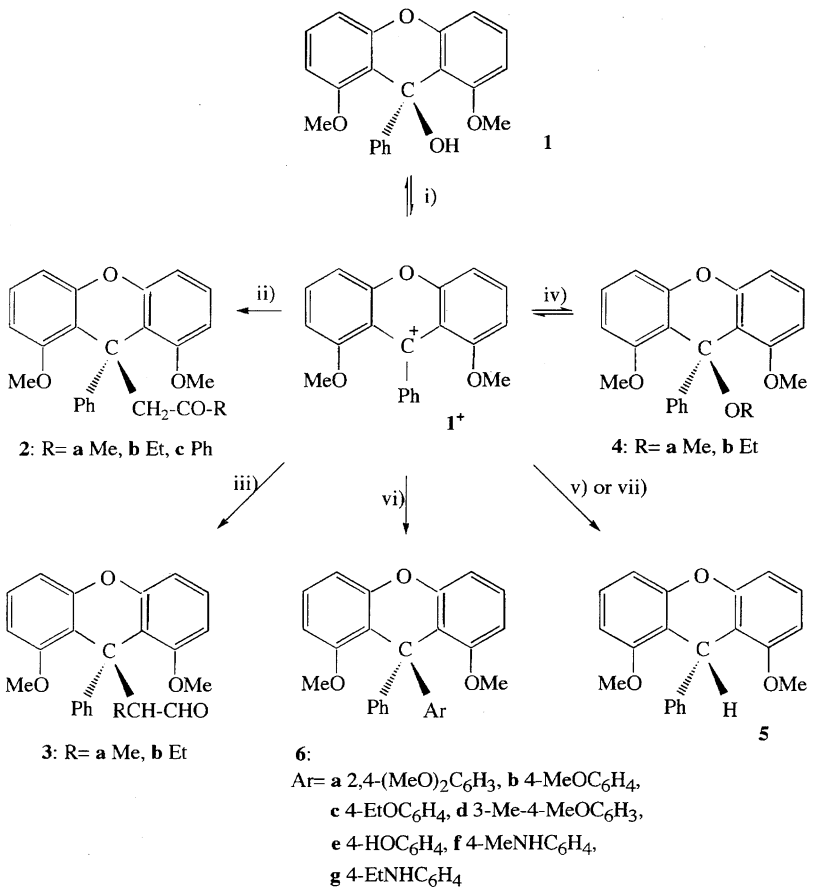
Reactions of 1,8-Dimethoxy-9-phenylxanthen-9-ol (1) with Ketones in the Presence of an Acid. With Acetone. A mixture of **1** (0.167 g, 0.5 mmol) and 60% aqueous perchloric acid (0.06 ml) in acetone (5 ml) was heated at 60 °C for 6 h to give a light-brown suspension. Water (10 ml) was added, and the precipitates were collected by filtration to give white crystals of 1,8-dimethoxy-9-phenylxanthen-9-ylmethyl methyl ketone (**2a**) in 96% yield. An analytical sample was obtained by recrystallization from propan-2-ol; mp 208—210 °C; IR 1720 cm^{-1} (C=O); MS *m*/*z* (%) 374 (M^+; 13), 317 ($M^+ - CH_2CMeO$; 100). Found: C, 76.65; H, 6.05%. Calcd for $C_{24}H_{22}O_4$: C, 76.99; H, 5.92%.

With Other Ketones. An analogous treatment of **1** in ethyl methyl ketone resulted in the formation of light-yellow crystals of 1,8-dimethoxy-9-phenylxanthen-9-ylmethyl ethyl ketone (**2b**) in 93% yield. The analytical sample was obtained by recrystallization from propan-2-ol; mp 164—166 °C; IR 1710 cm^{-1} (C=O); MS *m*/*z* (%) 388 (M^+; 9), 317 ($M^+ - CH_2CEtO$; 100). Found: C, 77.13; H, 6.25%. Calcd for $C_{25}H_{24}O_4$: C, 77.30; H, 6.23%.

An analogous treatment of **1** in acetophenone resulted in the formation of white crystals of 1,8-dimethoxy-9-phenylxanthen-9-ylmethyl phenyl ketone (**2c**) in 83% yield. An analytical sample was obtained by recrystallization from acetone; mp 245—246 °C; IR 1690 cm^{-1} (C=O); MS *m*/*z* (%) 436 (M^+; 6), 317 (100, $M^+ - CH_2CPhO$; 100). Found: C, 79.52; H, 5.69%. Calcd for $C_{29}H_{24}O_4$: C, 79.80; H, 5.54%.

An analogous treatment of **1** in diethyl ketone resulted to give **1** in 63% yield.

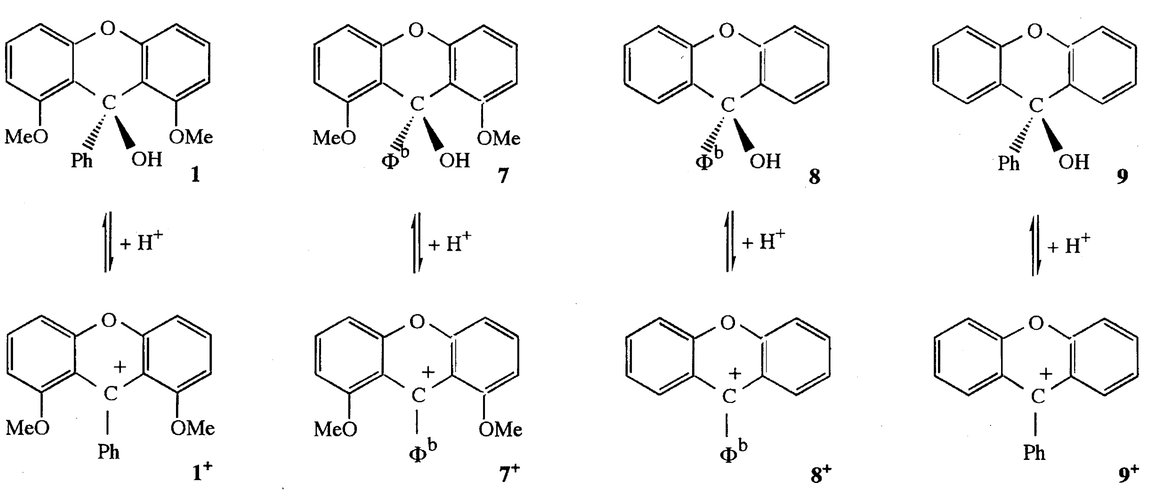
Reactions of 1,8-Dimethoxy-9-phenylxanthen-9-ol (1) with Aldehydes in the Presence of an Acid. With Propanal. A mixture of **1** (1 mmol), propanal (1 ml, 10 mmol), and 60% aqueous perchloric acid (0.12 ml) in 2-methylpropan-2-ol (10 ml) was heated



i) + H^+; ii) in CH_3CO-R, 60 °C, 6 h; iii) + RCH_2CHO in *t*-BuOH, 60 °C, 6 h; iv) in ROH, 50 °C, 5-18 h; v) in RR'CHOH, 50 °C, 0.5 h; vi) in ArH or + ArH in *t*-BuOH, 60-80 °C, 10-24 h; vii) + PhSH in *t*-BuOH, − PhSSPh.

Scheme 1.

$\Phi^b = 2,6\text{-}(MeO)_2C_6H_3$



pK_{R^+}= −0.81 1.14 4.80 0.75

Scheme 2.

Table 1. ^{1}H NMR Spectral Data[a] for 1,8-Dimethoxy-9-phenylxanthene Derivatives

Compound	3,6-H[b]	4,5-H[c]	2,7-H[c]	MeO[d]	Others[e,f]
2a	7.12	6.75	6.40	3.28	4.08s (CH_2), 1.08s (Me).
2b	7.11	6.75	6.40	3.27	4.00s (CH_2), 2.10q and 0.76t (Et).
2c	7.17	6.74	6.34	3.26	4.68s (CH_2).
3a	7.13	6.80, 6.74	6.44, 6.41	3.25, 3.16	9.37d (CHO), 4.1—4.0m (CH_2), 0.82d[7] (Me).
3b	7.16	6.81, 6.75	6.42, 6.41	3.21, 3.15	9.12d (CHO), 3.8—3.7m (CH_2), 0.9-1.0m (CH_2), 0.69t[8] (Me).
4a	7.15	6.81	6.51	3.38	2.96s (Me).
4b	7.14	6.78	6.49	3.40	3.04q[7] and 1.07t[7] (Et).
5	7.13	6.78	6.52	3.74	5.62s (CH).
6a	7.19	6.72	6.46	3.24	7.47d[8] (6″-H), 6.49d[8] (5″-H), 6.30d[3] (3″-H), 3.77s and 3.12s (2″,4″-MeO).
6b	7.15	6.77	6.46	3.20	7.38d[9] (2″,6″-H), 6.73d[9] (3″,5″-H), 3.74s (4″-MeO).
6c	7.15	6.77	6.46	3.20	7.36d[9] (2″,6″-H), 6.72d[9] (3″,5″-H), 3.97q[7] and 1.37t[7] (4″-EtO).
6d	7.14[g]	6.76	6.45	3.18	7.29d[2] (2″-H), 7.15[g](6″-H), 6.64d[9] (5″-H), 3.75s (4″-MeO), 2.12s (3″-Me).
6e	7.15	6.77	6.45	3.20	7.32d[9] (2″,6″-H), 6.64d[9] (3″,5″-H).
6f	7.14	6.76	6.49	3.20	7.42dd[9] (2″,6″-H), 6.45dd[8] (3″,5″-H), 2.79s (N–Me).
6g	7.13	6.76	6.45	3.19	7.42d[8] (2″,6″-H), 6.45d[8] (3″,5″-H), 3.09q[7] and 1.20t[7] (N–Et).

a) In $CDCl_3$ otherwise noted (δ/ppm; s = singlet, d = doublet, t = triplet, m = multiplet). b) Triplet with J_H = 7—8 Hz. c) Doublet or double doublets with J_H = 7—8 Hz and 1 Hz. d) Singlet. e) The coupling constants J_H greater than 2 Hz are given in square brackets in Hz, while those less than 2 Hz are omitted for clarity. f) The 9-phenyl proton resonances were observed at δ = 7.43—7.24 [multiplets, d or dd, J_H = 8 and 1 Hz, 2′,6′-H], 7.25—7.13 [t, J_H = 8 Hz, 3′,5′-H], and 7.08—6.98 [t, J_H = 7—8 Hz, 4′-H] ppm, otherwise given. g) Overlapped.

at 60 °C for 6 h to give light-brown suspension. Water (20 ml) was added, and the precipitates were collected by filtration to give white crystals of 2-(1,8-dimethoxy-9-phenylxanthen-9-yl)propanal (**3a**) in 93% yield. An analytical sample was obtained by recrystallization from acetone; mp 176—178 °C; IR 2720 [C(O) – H], 1720 and/or 1690 cm^{-1} (C=O); MS *m*/*z* (%) 317 (M$^+$ – CMeHCHO; 100). Found: C, 76.90; H, 6.02%. Calcd for $C_{24}H_{22}O_4$: C, 76.99; H, 5.92%.

With Butanal. An analogous treatment of **1** with butanal resulted in the formation of white crystals of 2-(1,8-dimethoxy-9-phenylxanthen-9-yl)butanal (**3b**) in 79% yield. An analytical sample was obtained by recrystallization from propan-2-ol; mp 168—170 °C; IR 2720 [C(O) – H], 1722 and/or 1718 cm^{-1} (C=O); MS *m*/*z* (%) 317 (M$^+$ – CEtCHO; 100).

Reactions of 1,8-Dimethoxy-9-phenylxanthen-9-ol (1) with Alcohols in the Presence of an Acid. With Methanol. A suspension of **1** (1 mmol) in methanol (10 ml) containing acetic acid (0.12 ml) was heated at 50 °C for 5 h to give a white suspension. Water (20 ml) was added, and the precipitates were collected by filtration to give white crystals of 9-phenyl-1,8,9-trimethoxyxanthene (**4a**) in 92% yield. An analytical sample was obtained by recrystallization from acetone; mp 228—229 °C; MS *m*/*z* (%) 348 (M$^+$; 12), 317 (M$^+$ – OMe; 100). Found: C, 75.72; H, 5.83%. Calcd for $C_{22}H_{20}O_4$: C, 75.84; H, 5.79%.

When **1** was heated in methanol in the absence of acetic acid (50 °C, 18 h), an analogous result was obtained to give **4a**.

An analogous treatment of **1** (1 mmol) in methanol (10 ml) containing 60% aqueous perchloric acid (0.06 ml) at 50 °C for 0.5 and 5 h resulted in the formation of a mixture of **1** and **4a** in 30 : 60 (0.5 h) or 19 : 76 (5 h) ratios.

With Ethanol. An analogous treatment of **1** in ethanol containing acetic acid resulted in the formation of 1,8-dimethoxy-9-ethoxy-9-phenylxanthene (**4b**) in 85% yield. An analytical sample was obtained by recrystallization from acetone; mp 175—176 °C; MS *m*/*z* (%) 362 (M$^+$; 7), 317 (M$^+$ – OEt; 100). Found: C, 76.01; H, 6.18%. Calcd for $C_{23}H_{22}O_4$: C, 76.22; H, 6.12%.

When **1** was heated in ethanol in the absence of acetic acid (50 °C, 18 h), an analogous result was obtained to give **4b**.

An analogous treatment of **1** (1 mmol) in ethanol (10 ml) containing 60% aqueous perchloric acid (0.06 ml) at 50 °C for 0.5 h resulted in the formation of 1,8-dimethoxy-9-phenylxanthene (**5**) in 93% yield. An analytical sample was obtained by recrystallization from acetone; mp 219—222 °C; MS *m*/*z* (%) 318 (M$^+$; 19), 241 (xanthenium$^+$; 100). Found: C, 78.87; H, 5.78%. Calcd for $C_{21}H_{18}O_3$: C, 79.22; H, 5.70%.

In 2-Propanol. An analogous treatment of **1** in propan-2-ol containing acetic acid (or in the absence of acid) resulted in the formation of a mixture of **1**, possibly 9-(isopropxy)-1,8-dimethoxy-9-phenylxanthene (**4c**), and **5** in 26 : 69 : 5 ratio (or 43 : 56 : 1 in the absence of acetic acid); MS of **4c**: *m*/*z* (%) 376 (M$^+$; 3), 317 (M$^+$ – O^{i}Pr; 100).

An analogous treatment of **1** in propan-2-ol containing 60% aqueous perchloric acid at 50 °C for 0.5 h resulted to give **5** in 97% yield.

Reactions of 1,8-Dimethoxy-9-phenylxanthen-9-ol (1) with Aromatic Compounds in the Presence of an Acid. With 1,3-Dimethoxybenzene. To a suspension of **1** (1 mmol) in 1,3-dimethoxybenzene (10 ml) was added trifluoroacetic acid (0.10 ml,

Table 2. ^{13}C NMR Spectral Data a) for 1,8-Dimethoxy-9-phenylxanthene Derivatives

Compounds	δ/ppm; in $CDCl_3$
2a	157.3, 150.5, 128.2, 116.5, 109.3, 107.3; 41.8; 55.7; —,c) 127.9, 126.4, 124.5, — (C=O),c) 48.0, 31.0.
2b	157.2, 150.5, 128.1, 116.6, 109.3, 107.2, 41.8; 55.6; 150.7, 127.9, 126.3, 124.4; 210.0 (C=O), 46.5, 37.0, 7.5.
2c	157.1, 150.8, 128.1, 116.9, 109.3, 107.2, 42.0; 55.6; 150.8, 127.8, 126.4, 124.5; 198.8 (C=O), 138.3, 132.2, 128.0, 42.8.
3a	157.6 and 156.8, 151.7 and 150.4, 128.5, 116.4 and 113.2, 109.4 and 109.2, 107.7 and 106.8, 48.2; 55.4 and 54.5; 150.1, 128.9, 128.6, 126.2, 124.3; 203.4 (C=O), 50.0, 12.4 (Me).
3b	157.7 and 156.9, 151.6 and 150.7, 128.5, 116.9 and 113.9, 109.5 and 109.1, 108.0 and 106.9, 47.9; 55.5 and 54.6; 150.6, 128.8, 128.6, 126.2, 124.3; 204.6 (C=O), 57.4, 20.2 and 11.9 (Et).
4a	159.1, 151.7, 129.4, 113.0, 108.8, 107.4, 75.6; 56.1; 149.0, 127.0, 125.9, 124.9; 51.4.
4b	159.2, 151.4, 129.2, 113.9, 108.7, 107.2, 74.7; 55.9; 149.3, 127.1, 125.8, 124.8; 59.4, 15.7.
5	157.3, 152.6, 127.7, 115.0, 109.2, 105.1, 34.1; 55.7; 145.6, 128.3, 127.8, 125.8.
6a	157.7, 151.0, 127.5, 119.3, 109.2, 107.5, 48.2; 55.3; 158.4, 158.2, 145.3, 130.9, 130.1, 129.3, 127.5, 127.3, 125.7, 103.2, 100.1, 56.1 (2″-MeO), 55.7 (4″-MeO).
6b	157.9, 150.4, 128.1, 119.4, 109.4, 107.9, 50.1; 55.4; 157.1, 148.1, 138.6, 130.2, 129.0, 126.5, 124.7, 112.2, 55.1 (4″-MeO).
6c	157.9, 150.4, 128.1, 119.4, 109.3, 107.9, 50.1; 55.4; 156.5, 148.0, 138.5, 130.2, 129.0, 126.5, 124.7, 112.8, 63.2 and 14.9 (4″-EtO).
6d	158.0, 150.4, 128.0, 119.6, 109.4, 108.0, 50.1; 55.4; 155.4, 148.6, 137.7, 131.6, 129.1, 127.6, 126.4, 124.6, 124.4, 108.5, 55.1 (4″-MeO), 16.6 (3″-Me).
6e	157.9, 150.4, 128.1, 119.3, 109.4, 107.9, —;c) 55.4; 153.0, 147.9, 139.0, 130.4, 129.1, 126.6, 124.8, 113.7.
6f	158.0, 150.4, 127.9, 119.7, 109.3, 108.0, 50.1; 55.5; 149.1, 146.8, 134.8, 130.0, 129.1, 126.2, 124.4, 111.3, 30.8 (N–Me).
6g	158.0, 150.4, 127.8, 119.7, 109.3, 108.0, —;c) 55.4; 149.0, 146.0, 134.8, 130.0, 129.1, 126.2, 124.4, 111.6, 38.6 and 15.0 (N–Et).

a) In the order of xanthene ring carbons (1, 8-C, C–O–C, 3, 6-C, bridge C, 4, 5-C, 2, 7-C, 9-C); 1,8-MeO; 9-phenyl carbons; and others. c) The resonance is too weak to be observed or overlapped.

1.2 mmol) to give a dark-brown solution. It was heated at 80 °C for 24 h to give a light-brown solution, hexane (20 ml) was added, and the mixture was cooled at −30 °C to give colorless crystals of 1,8-dimethoxy-9-(2,4-dimethoxyphenyl)-9-phenylxanthene (**6a**) in 89% yield. An analytical sample was obtained by recrystallization from acetone; mp 194—196 °C; MS *m/z* (%) 454 (M$^+$; 38), 377 (M$^+$ − Ph; 100), 317 (M$^+$ − $C_6H_3(OMe)_2$; 20). Found: C, 76.47; H, 5.92%. Calcd for $C_{29}H_{26}O_5$: C, 76.63; H, 5.77%.

With Methoxybenzene. A mixture of **1** (0.5 mmol) and trifluoroacetic acid (0.06 ml) in methoxybenzene (5 ml) was heated at 80 °C for 10 h. The resulting light-brown solution was treated as mentioned above to give colorless crystals of 1,8-dimethoxy-9-(4-methoxyphenyl)-9-phenylxanthene (**6b**) in 65% yield. An analytical sample was obtained by recrystallization from acetone; mp 194—196 °C; MS *m/z* (%) 424 (M$^+$; 43), 347 (M$^+$ − Ph; 100), 317 (M$^+$ − C_6H_5OMe; 69). Found: C, 79.19; H, 5.76%. Calcd for $C_{28}H_{24}O_4$: C, 79.22; H, 5.70%.

With Ethoxybenzene. A mixture of **1** (0.5 mmol) and trifluoroacetic acid (0.06 ml) in ethoxybenzene (5 ml) was heated at 80 °C for 24 h. The resulting light-brown solution was treated as mentioned above to give white crystals of 9-(4-ethoxyphenyl)-1,8-dimethoxy-9-phenylxanthene (**6c**) in 74% yield. An analytical sample was obtained by recrystallization from propan-2-ol; mp 183—185 °C; MS *m/z* (%) 438 (M$^+$; 45), 361 (M$^+$ − Ph; 100), 317 (M$^+$ − C_6H_5OEt; 83). Found: C, 79.21; H, 6.12%. Calcd for $C_{29}H_{26}O_4$: C, 79.43; H, 5.98%.

With 2-Methoxytoluene. A mixture of **1** (0.5 mmol) and trifluoroacetic acid (0.06 ml) in 2-methoxytoluene (5 ml) was heated at 80 °C for 24 h. The resulting light-brown solution was treated as mentioned above to give white crystals of 1,8-dimethoxy-9-(4-methoxy-3-methylphenyl)-9-phenylxanthene (**6d**) in 72% yield. An analytical sample was obtained by recrystallization from acetone; mp 183—184 °C; MS *m/z* (%) 438 (M$^+$; 32), 361 (M$^+$ − Ph; 85), 317 (M$^+$ − $C_6H_3Me(OMe)$; 95), 91 ($PhCH_2^+$; 100). Found: C, 79.21; H, 6.06%. Calcd for $C_{29}H_{26}O_4$: C, 79.43; H, 5.98%.

With Phenol. A mixture of **1** (0.5 mmol) and trifluoroacetic acid (0.06 ml, 0.6 mmol) in phenol (5 ml) was heated at 80 °C for 24 h to give a light-brown solution. Hexane (10 ml) was added, and the mixture was cooled at −30 °C to give white crystals of 4-(1,8-dimethoxy-9-phenylxanthen-9-yl)phenol (**6e**) in 93% yield. An analytical sample was obtained by recrystallization from propan-2-ol; mp 210—213 °C; IR 3400 cm^{-1} br (OH); MS *m/z* (%) 410 (M$^+$; 30), 333 (M$^+$ − Ph; 100), 317 (M$^+$ − C_6H_4OH; 65), 91 ($PhCH_2^+$; 85). Found: C, 78.72; H, 5.57%. Calcd for $C_{27}H_{22}O_4$: C, 79.01; H, 5.40%.

With *N*-Methylaniline. A mixture of **1** (0.5 mmol), *N*-methylaniline (0.54 ml, 5 mmol), and 60% aqueous perchloric acid (0.06 ml) in 2-methylpropan-2-ol (5 ml) was heated at 60 °C for 10 h to give a light-brown suspension. Water (10 ml) was added, and the precipitates were collected by filtration to give 1,8-dimethoxy-

9-(4-methylaminophenyl)-9-phenylxanthene (**6f**) in 99% yield. An analytical sample was obtained by recrystallization from acetone; mp 228—230 °C MS *m*/*z* (%) 423 (M^+; 99.5), 346 (100, $M^+ - Ph$; 100), 317 ($M^+ - C_6H_5NMeH$; 50). Found: C, 79.31; H, 6.07; N 3.37%. Calcd for $C_{28}H_{25}NO_3$: C, 79.41; H, 5.95; N 3.31%.

With *N*-Ethylaniline. The treatment of an analogous mixture of **1**, *N*-ethylaniline, and 60% aqueous perchloric acid in 2-methylpropan-2-ol resulted in the formation of an 87 : 13 mixture of 9-(4-ethylaminophenyl)-1,8-dimethoxy-9-phenylxanthene (**6g**) and **5**; MS of **6g** *m*/*z* (%) 437 (M^+; 100), 360 ($M^+ - Ph$; 89).

With Benzenethiol. The treatment of an analogous mixture of **1** (0.5 mmol), benzenethiol (0.06 ml, 0.6 mmol), and 60% aqueous perchloric acid (0.06 ml) in 2-methylpropan-2-ol (5 ml) resulted in the formation of a 49 : 51 mixture of **5** and diphenyl disulfide in 78 and 80% yields, respectively, as characterized by the GC-MS and ^{1}H NMR spectra.

Preparation of 9-Arylxanthen-9-ols (7—9). 9-(2,6-Dimethoxyphenyl)-1,8-dimethoxyxanthen-9-ol (7). Compound **7** was prepared as described elsewhere.[6,7]

9-(2,6-Dimethoxyphenyl)xanthen-9-ol (8). To a mixture of 15% hexane solution of butyllithium (12 ml, 19.2 mmol) and 1, 3-dimethoxybenzene (2.7 ml, 20.4 mmol) was added a catalytic amount of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (0.075 ml) at 0 °C under argon. The mixture was stirred at room temperature for 2 h to give a white suspension of 2,6-dimethoxyphenyllithium. Toluene (70 ml) was added followed by xanthone (2.94 ml, 15 mmol); the mixture was stirred for 24 h at room temperature. Hexane (120 ml) and methanol (2 ml) were added at 0 °C. The resultant precipitates were separated, washed well with water, and recrystallized from propan-2-ol to give white crystals of **8** in 86—73% yield; mp 189—190 °C; ^{1}H NMR δ = 7.65 [s, 1H, OH], 7.36 [dd, J = 8 and 2 Hz, 2H, 1,8- or 4,5-H], 7.22 [dt, J = 8 and 2 Hz, overlapped, 2,7- or 3, 6-H], 7.20 [t, J = 8 Hz, overlapped, 4′-H], 7.12 [dd, J = 8 and 1.5 Hz, 2H, 4,5- or 1,8-H], 6.98 [dt, J = 8 and 1.5 Hz, 3,6- or 2,7-H], 6.58 [d, J = 8 Hz, 2H, 3′,5′-H], 3.56 [s, 6H, 2′,6′-MeO]; ^{13}C NMR δ = 157.3 [s, 2′,6′-C], 149.5 [s, C–O(10)], 128.9 [d, 4′-C], 128.4 [s, C–C(9)], 128.3 [d, overlapped], 128.0 [d, overlapped], 123.9 [s, 1′-C], 122.4 [d], 115.5 [d], 106.7 [d; 3′,5′-C], 71.75 [s; 9-C], and 56.5 [t; 2′,6′-MeO]. Found: C, 75.32; H, 5.50%. Calcd for $C_{21}H_{18}O_4$: C, 75.43; H, 5.43%.

9-Phenylxanthen-9-ol (9). Compound **9**[8—10] was prepared essentially in an analogous manner as above by the reaction of phenyllithium, prepared from a 15% hexane solution of butyllithium and bromobenzene, with xanthone.

Preparation of 9-(2,6-Dimethoxyphenyl)xanthen-9-ylium Perchlorate (8^+). To a solution of **8** (0.334 g, 1 mmol) in acetone (10 ml) was added 60% aqueous perchloric acid (0.12 ml, 1.3 mmol) to give a dark-red solution. After the mixture was stirred at room temperature for 1 h, it was cooled at −30 °C overnight to give dark-red crystals of 8^+ in 80% yield; mp was not observed below 260 °C; IR 1099 cm^{-1} (ClO_4); ^{1}H NMR δ = 8.55 [t, J = 9 Hz, 2H, overlapped, 2,7- or 3,6-H], 8.54 [d, J = 9 Hz, 2H, overlapped, 1,8- or 4,5-H], 8.05 [d, J = 8 Hz, 2H, 4,5- or 1,8-H], 7.95 [t, J = 8 Hz, 2H, 3,6- or 2,7-H], 7.72 [t, J = 8 Hz, 1H, 4′-H], 6.89 [d, J = 8 Hz, 2H, 3′,5′,-H], and 3.67 [s, 6H, 2′,6′-MeO].

Measurement of pK_{R^+}. Compounds **1**, **7**—**9** are soluble in concentrated hydrochloric acid. They were dissolved in the minimum amount of the acid and were diluted with water or with a dilute aqueous sodium hydroxide to 1.0×10^{-4} M (1 M = 1 mol dm^{-3}) of 1^+, 7^+—9^+. The UV-vis data are summarized in Table 3. Their pK_{R^+} values [Eq. 1] were evaluated for the solutions by titration with water or dilute aqueous sodium hydroxide monitoring the UV-vis spectra at 290, 280, 375, or 374 nm, respectively. The basicities are the mean pH values (±0.1) of three- to five-times measurements when the concentrations of R^+ diminished to 0.5×10^{-4} M. The results are given in Scheme 2.

$$pK_{R^+} = pH + \log [R^+]/[ROH] \qquad (1)$$

Table 3. UV-vis Data for Xanthen-9-ylium Ions in Hydrochloric Acid

Xanthen-9-ylium Ion	λ_{max}/nm	$\log \varepsilon$
1^+	290	4.46
	357	4.07
	461	3.87
7^+	280	4.44
	356	4.27
	450	3.95
8^+	(347)	(4.11)[a]
	375	4.34
	446	3.65
9^+	255	4.32
	374	4.27
	450	3.52

a) Shoulder.

Results and Discussion

Reactions of 1,8-Dimethoxy-9-phenylxanthen-9-ol (1) with Ketones and Aldehydes in the Presence of an Acid. 9-Phenylxanthen-9-ylium perchlorate (9^+) has been known to react with active methylene compounds, such as 2,4-pentanedione, to give 3-(9-phenylxanthen-9-yl)-pentane-2,4-dione.[8] We recently reported that bis(2,6-dimethoxyphenyl)methanol, $\Phi^b{}_2$CHOH, reacted in the presence of a catalytic amount of acid with a variety of carbonyl compounds, such as acetone, ethyl methyl ketone, diethyl ketone, acetophenone, propanal, and butanal, to give new ketones, $\Phi^b{}_2$CH–CHR–CO–R′.[5] Compound **1** also reacted with acetone in the presence of a catalytic amount of acid to give white crystals of a new ketone (**2a**) in a good yield. The formation of **2a** can be understood to be caused by a reaction of the carbenium ion 1^+ with the enol form of acetone [Eq. 2]. The reverse reaction has been observed in the photolysis of 3-(xanthen-9-yl)-pentane-2,4-dione.[11] While $\Phi^b{}_2$CHOH reacted with ethyl methyl ketone to give an 80 : 20 mixture of $\Phi^b{}_2$CH–CHMe–CO–Me and $\Phi^b{}_2$CH–CH_2–CO–Et,[5] compound **1** reacted to give only one product (**2b**), where the methyl carbon reacted selectively, probably due to a steric reason. In fact, **1** was inert against diethyl ketone. Compound **1** also reacted with methyl phenyl ketone to give an analogous ketone (**2c**). In strong contrast, we confirmed that 1,8-dimethoxy-9-(2,6-dimethoxyphenyl)xanthen-9-ylium (7^+) and 9-(2,6-dimethoxyphenyl)xanthen-9-ylium (8^+) were inert against these ketones, probably due to a steric hindrance of the methoxy substituents on the 9-phenyl group.

$$RCH_2\text{–CO–}R' \overset{K_E}{\rightleftarrows} RCH\text{=}CR'\text{–OH} \qquad (2)$$

Triphenylcarbenium ion and triarylcarbenium ions of type $[\mathrm{Ar}\Phi_2^{\mathrm{b}}\mathrm{C}]^+$ (Ar = Ph, Φ^{b}) have been known to be inert against acetone.[1,2,12,13] Bis(4-methoxyphenyl)methanol has been reported to react with acetone in the presence of an acid to give bis(4-methoxyphenyl) ketone and propan-2-ol, where the diarylmethanol was oxidized by acetone.[14] On the other hand, some diarylchloromethanes have been reported to react with alkenes and alkynes in the presence of a Lewis acid to give addition products.[15]

Reactions of **1** with aldehydes, such as propanal and butanal, in hot 2-methylpropan-2-ol, also gave analogous products (**3a**) and (**3b**). The relative reactivity of these ketones was compared by measuring the relative rations of **1** : **2** or **3** of the products of **1** heated in 2-methylpropan-2-ol containing ketone or aldehyde and perchloric acid at 60 °C for 6 h. The ratio (%) of **2** or **3** decreased in the order of **3b** (93)≈**2c** (91) > **3a** (79) > **2a** (63) > **2b** (28).

Reactions of 1,8-Dimethoxy-9-phenylxanthen-9-ol (1) with Alcohols in the Presence of an Acid. Compound **1** reacted in hot methanol and ethanol in the absence of acid to give the ethers (**4a**,**b**). Analogous results were obtained in hot alcohols in the presence of a weak acid, like acetic acid. However, **1** reacted in propan-2-ol to give a mixture containing the reduced compound (**5**). When **1** was heated for a short period (0.5 h at 50 °C) in these primary and secondary alcohols in the presence of a slight excess of strong acid, like perchloric acid, **5** was obtained in quantitative yields. Such a reduction by alcohols has often been observed for $[\mathrm{Ar}\Phi_2\mathrm{C}]\mathrm{X}$ and $[\Phi_2\mathrm{CH}]\mathrm{X}$, and the aldehyde or ketone were detected as the by-product [Eqs. 3 and 4].[1,2,5] The related reductions of common triarylcarbenium ions by alcohol have been known in some cases.[16,17] Olah and Svoboda reported that triphenylcarbenium ion was reduced by a variety of organic compounds, such as ethers, aldehydes, amines, and formic acid.[18] Hori et al. reported that **9** was reduced in ethanol containing hydrochloric acid to give 9-phenylxanthene.[10] In strong contrast, again, **7** and **8** were inert against these alcohols under analogous conditions used for **1**, although **7** has been reported to be reduced by triethylsilane upon heating for prolonged hours in acetic acid.[7]

The relative reactivity of these alcohols with **1** was compared by measuring the relative ratios of **1** and **5** in the reaction mixture of **1** heated in 2-methylpropan-2-ol containing alcohol and perchloric acid at 60 °C for 2 h. The ratio (%) of **5** decreased in the order, propan-2-ol (65) > ethanol (33) > butan-1-ol (24) > propan-1-ol (19) > 1-methylpropan-1-ol (15), which may be compared with the orders for $\Phi_2\mathrm{CHOH}$: propan-2-ol > 2-methylpropan-1-ol > ethanol > propan-1-ol > butan-1-ol > methanol,[5] and for $\mathrm{Ph}\Phi_2\mathrm{COH}$: ethanol > butan-1-ol > propan-1-ol > 1-methylpropan-1-ol > 2-methylpropan-1-ol.[1] The reactivity [Eqs. 3 and 4] must be affected by both the reducing ability and the bulkiness of alcohols, R′R″CHOH,[1,2,5] and by the stability (K_{R^+}) and the oxidizability including the steric effect of carbenium ion, $[\mathrm{RAr_2C}]^+$, (see below).

$$\mathrm{RAr_2C{-}OH} + \mathrm{H}^+ \xrightleftharpoons{1/K_{\mathrm{R}^+}} [\mathrm{RAr_2C}]^+ + \mathrm{H_2O} \tag{3}$$

$$[\mathrm{RAr_2C}]^+ + \mathrm{R'R''CHOH} \xrightarrow{k_2} \mathrm{RAr_2C{-}H} + \mathrm{R'R''CO} + \mathrm{H}^+ \tag{4}$$

Reactions of 1,8-Dimethoxy-9-phenylxanthen-9-ol (1) with Aromatic Compounds in the Presence of an Acid. Xanthen-9-ylium ions are expected to react with electron-rich aromatic compounds.[19] In fact, Hori et al. also reported that $\mathbf{9}^+$ reacted with aniline to give 9-(*p*-aminophenyl)-9-phenylxanthene and with phenol to give 9-(*p*-hydroxyphenyl)-9-phenylxanthene.[10] Diarylmethanol $\Phi^{\mathrm{b}}{}_2\mathrm{CHOH}$ reacted with 1,3-dimethoxybenzene in the presence of an acid to give 2,4-dimethoxyphenylbis(2,6-dimethoxyphenyl)methane.[5] It has also been known that irradiation of a variety of carbenium ions, including $\mathbf{9}^+$ in the presence of methoxybenzenes, resulted in electron transfer from the methoxybenzenes to carbenium ions to give the corresponding radicals.[20,21] Thus, we treated **1** with a variety of aromatic compounds in the presence of an acid. When a suspension of **1** in 1,3-dimethoxybenzene was heated in the presence of a slight excess of trifluoroacetic acid, colorless crystals of 1,8-dimethoxy-9-(2,4-dimethoxyphenyl)-9-phenylxanthene (**6a**) were obtained in good yield. Under an analogous condition, **1** did not react with 1,3,5-trimethoxybenzene, probably due to the bulkiness, but analogous reactions were observed with methoxybenzene, ethoxybenzene, 2-methoxytoluene, phenol, and *N*-methylaniline to give the 9-*p*-substituted phenyl derivatives (**6b**—**6f**). Benzene, toluene, *o*-xylene, *p*-xylene, chlorobenzene, and bromobenzene were inert, probably due to the weak nucleophilicity. With *N*-ethylaniline, an 87 : 13 mixture of C-bonded derivative (**6g**) and the reduced compound **5** was obtained. The fate of the oxidized product of *N*-ethylaniline is unknown at present. Benzenethiol also reduced **1** in the presence of acid to give **5** and diphenyl disulfide, selectively.

Compounds **7** and **8** were inert, again, with these aromatic compounds.

In the GC-MS spectra, the parent peaks were observed for all the 9,9-diaryl-1,8-dimethoxyxanthenes (**6a**—**g**), suggesting their high thermal stability. Preliminary experimentals have shown that these compounds are highly fluorescent.

Basicity of 1,8-Dimethoxy-9-phenylxanthen-9-ol (1). The basicity of alcohol or the stability of the carbenium ion is defined by the equilibrium constant ($\mathrm{p}K_{\mathrm{R}^+}$) of the proton-alcohol reaction in water, such as given in Eq. 3.[22] The basicity of 9-arylxanthen-9-ol is often affected not only by the electronic, but also by the steric effects of both the xanthenol and the xanthenylium ion.[22—24] It is often measured in a water-acetonitrile mixed solvent due to the solubility problem. Fortunately, compounds **1** and **7**—**9**, shown in Scheme 2, were soluble in hydrochloric acid, and their basicities could be measured in dilute hydrochloric acid. Due to the relief of a nonbonding interaction, *ortho*-substitution on the phenyl group in 9-phenylxanthen-9-ol causes, in general, enhanced stabilization of the xanthenylium ions.[23,24] In fact, **8** ($\mathrm{p}K_{\mathrm{R}^+} = 4.80$), an isomer of **1**, was found to be the most basic among the four 9-arylxanthen-9-ols in Scheme 2, and **7** (+1.14; +2.5[6]) was more basic than **1** (−0.81). We conclude from these results that the drastic differences in the reactivities between **1** and **7** or **8** are due to a steric effect, rather than an electronic effect of *ortho*-methoxy substituents. We were interested in the effect of the 1,8-dimethoxy groups in 9-arylxanthen-9-ols, since the substituents would increase the stability of xanthenylium by a π-electron-donation, or would interfere by a steric interaction with the π-conjugation of 9-aryl group with the xanthenylium π-system. Ethoxy-group substitution at the 1,8-positions of xanthenol has been reported to increase the basicity of 1,8-diethoxyxanthen-9-ol (+1.38),[25] as compared with that of xanthen-9-ol (−0.17;[25] −0.2[22]). The basicity of 1,3,6,8-tetramethoxyxanthen-9-ol has been reported to be very high (+6.0).[22] In strong contrast, **1** was less basic than **9** (+0.75, Scheme 2; +1.8[22]), and **7** was less basic than **8**. These observations possibly indicate the presence of interference of the π-conjugation of 9-aryl group with the xanthenylium π-system. Measurements of reduction potentials of these xanthenylium ions, as well as their chemical reductions, are under investigation, which may distinguish the steric effect and the electronic effect of 1,8-dimethoxy groups.

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