The Oxidation of (*E*)-α-Phenylcinnamic Acids with Manganese(III) Acetate

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The oxidation of eight (*E*)-α-phenylcinnamic acids with manganese(III) acetate in boiling acetic acid containing acetic anhydride gave 3-phenylcoumarins, 3-phenyl-1-oxaspiro[4.5]deca-3,7,9-triene-2,6-diones, 2-phenylbenzofurans, 3-(acetoxymethyl)-2-phenylbenzofurans, 3-formyl-2-phenylbenzofuran, 2-acetoxy-2-phenyl-3(2*H*)-benzofuranones, (*Z*)-α-acetoxystilbenes, 2-acetoxy-1,2-diphenylethanones, 5-acetoxy-4,5-diphenyl-2(5*H*)-furanones, and diphenylacetylene. The reaction pathways are discussed.

In the reaction of lead(IV) acetate and manganese(III) acetate with phenolic compounds in which a hydroxyl group and a double bond are located in spatially suitable positions, an oxidative cyclization has often been observed.[1-7] Davies *et al.* have reported that 2′-substituted biphenyl-2-carboxylic acid was oxidized with lead(IV) acetate to give 3,4-benzocoumarin as a cyclized product.[8] This result prompted us to examine the oxidation of α-phenylcinnamic acids with manganese(III) acetate, in the hope to obtain 3-phenylcoumarins.

(*E*)-α-Phenylcinnamic acids (**1a**—**h**) were prepared from the corresponding phenylacetic acid and benzaldehyde by the Perkin condensation; the (*Z*)-acid (**2f**) was also obtained in the reaction as a minor product. The structures of the new α-phenylcinnamic acids were confirmed by examining their NMR[9] and IR spectra, and by elemental analyses. The (*E*)-α-phenylcinnamic acids which were examined were (*E*)-2-methoxy-α-phenylcinnamic acid (**1a**), (*E*)-2,4-dimethoxy-α-phenylcinnamic acid (**1b**), (*E*)-2,3,4-trimethoxy-α-phenylcinnamic acid (**1c**), (*E*)-2-methoxy-α-(2-methoxyphenyl)-cinnamic acid (**1d**), (*E*)-2,4-dimethoxy-α-(2-methoxyphenyl)cinnamic acid (**1e**), (*E*)-2-methoxy-α-(4-methoxyphenyl)cinnamic acid (**1f**), (*E*)-2,4-dimethoxy-α-(4-methoxyphenyl)cinnamic acid (**1g**), and (*E*)-3,4-dimethoxy-α-(4-methoxyphenyl)cinnamic acid (**1h**). When the (*E*)-α-phenylcinnamic acids (**1a**—**h**) were oxidized with manganese(III) acetate, several products (**3**—**12**) were isolated. The structures of the products were determined again by examining their NMR, IR, and mass spectra, by elemental analyses, and by unambiguous syntheses.

The reactions of **1a**—**h** were carried out using two, four, and five equivalents of manganese(III) acetate in acetic acid containing acetic anhydride at the reflux temperature until the color of manganese(III) acetate disappeared (Fig. 1 and Table 1).

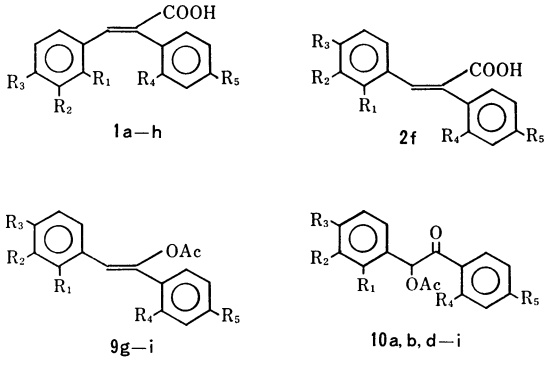
*3-Phenylcoumarins (**3**) and Spiro Lactones (**4**).* The manganese(III) acetate oxidation of methoxy-substituted (*E*)-α-phenylcinnamic acids (**1**), in which α- and β-phenyl groups are *cis*, afforded 3-phenylcoumarins (**3**) and spiro lactones (**4**), both with a *trans* double bond as to two phenyl groups in **3** and the six-menbered ring and a phenyl group in **4**. This indicates that the isomerization of **1** to **2** is involved and that then **2** is oxidized with manganese(III) acetate to give a carbonyloxy radical (I). Subsequently, the (I) radical cyclizes either at the 2-position with the elimination of a methoxyl radical, or at the 6-position with the elimination of hydrogen, while the attack at the 1-position yields **4** with the elimination of the methyl radical (Scheme 1). The pathway would be similar to that of the oxidation of 2′-substituted biphenyl-2-carboxylic acid with lead(IV) acetate.[8] It seems that the cyclization can occur when **1** possesses more than two methoxyl groups in the β-phenyl moiety (**1b**, **1c**, **1e**, and **1h**). An exception is **1g**.

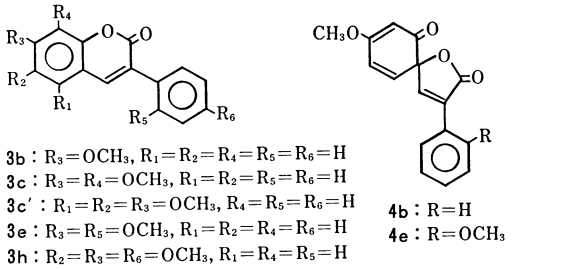
*2-Phenylbenzofurans (**5**), 3-(Acetoxymethyl)-2-phenylbenzofurans (**6**), 3-Formyl-2-phenylbenzofuran (**7**), and 2-Acetoxy-2-phenyl-3(2H)-benzofuranone (**8**).* These compounds were obtained in the reaction of **1** substances which have a methoxyl group at the 2-position in the β-phenyl ring (**1a**, **1b**, **1d**, **1e**, **1f**, and **1g**). An exception is **1c**. Thus, the reaction may proceed through the pathway shown in Scheme 2. The vinylic radical (II), which is formed on the oxidative decarboxylation of the parent acid (**1**), is further oxidized to give a vinylic cation (III). The 2-methoxyl group in **1** attacks the cationic center of III intramolecularly, and then **5** is formed by the removal of the methyl cation. A similar reaction has been known to occur in the solvolysis of 1-aryl-2,2-bis(2-methoxyphenyl)vinyl halides.[10] In the oxidation of **1f**, the yield of **5f** decreased from 34 to 15%, and that of **6f** increased from 2 to 14%, where the amount of manganese(III) acetate was increased, and **7** and **8f** were isolated in the reaction in a molar ratio of 1:5 (Table 1, entries 8 and 9). This suggests that **6f**, **7**, and **8f** can be formed *via* the oxidation of **5f**. In fact, when 2-phenylbenzofuran (**5a**) was oxidized with manganese(III) acetate, 3-(acetoxymethyl)-2-phenylbenzofuran (**6a**, 30%) and 2-acetoxy-2-phenyl-3(2*H*)-benzofuranone (**8a**, 25%) were obtained. Therefore, the reaction may proceed as shown in Scheme 2. **7** can be formed by the further oxidation of **6**, followed by hydrolysis during the work-up. Acetoxymethylation has been reported to occur in the reaction of aromatic compounds with manganese(III) acetate.[11-15]

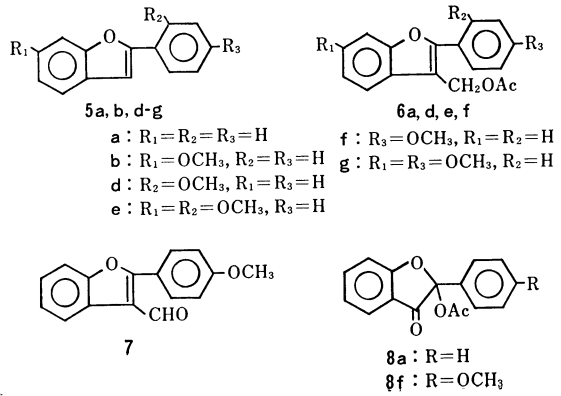
*(Z)-α-Acetoxystilbenes (**9**), 2-Acetoxy-1,2-diphenylethanones (**10**), and 5-Acetoxy-4,5-diphenyl-2(5H)-furanone (**11**).* The structures of **9** were elucidated by a comparison of their UV spectra with those of (*E*)- and (*Z*)-α-acetoxystilbenes.[16] (*Z*)-α-Acetoxy-3′,4,4′-trimethoxystilbene (**9h**) was synthesized from the corresponding benzyl aryl ketone and was found to be identical. The reaction which gave **9** may proceed through one of the following pathways: a) an acetoxyl radical attacks the vinylic radical (II) to form **9**, or b) the vinylic cation (III) reacts with acetic acid to yield **9**, with the elimination of a proton. The absence of dimeric compounds and stilbenes, which could be

formed from II, in the products suggests that the b pathway is preferable to the a pathway. As to the formation of **10**, again two pathways can be considered: c) the oxidation of **9** gives **10**, or d) the oxidation of benzyl aryl ketone, which might be formed *via* the solvolysis of **9**, gives **10**. In order to distinguish the c and d pathways, **9h** was oxidized with two equivalents of manganese(III) acetate. 2-Acetoxy-1-(4-methoxyphenyl)-2-(3,4-dimethoxyphenyl)ethanone (**10h**) was obtained in a good yield (67%), together with unchanged **9h** (22%) (Table 2, entry 1). However, when **9h** was heated without the oxidant, **9h** was recovered quantitatively. The fact that 3,4-dimethoxybenzyl 4-methoxyphenyl ketone, which might be formed by the solvolysis of **9h**, was not found in the products of these reactions, even though a substantial amount of **9h** was recovered, leads to the conclusion that the 2-acetoxy-1,2-diphenylethanones (**10**) were formed through the c pathway. It is worth noting that the acetoxyl group in 2-acetoxy-1,2-diphenylethanone (**10**) obtained in the reaction of (*E*)-α-phenylcinnamic acid was located at the α-position in the parent acids and that the yield of **10i** was much improved in the reaction of **9i** in acetic acid (Table 2, entry 4). This suggests that the manganese(III) acetate oxidation of **1** can be utilized as a regiospecific synthesis of 2-acetoxy-1,2-diphenylethanones which have different aryl groups from (*E*)-α-phenylcinnamic acids (**1**), although the formation of α-acetoxy ketones from enol acetates by lead(IV) acetate[17] and by anodic oxidation[18] have been reported.

When **9h** was oxidized with five equivalents of manganese(III) acetate, 3,4,4′-trimethoxybenzil (**13h**) was obtained, together with **10h** (Table 2, entry 2). Two reaction pathways (e and f) which could give **13h** may be envisaged: e) the oxidation of **9h** gives **13h**, or f) the oxidation of 2-acetoxy-1-(4-methoxy-







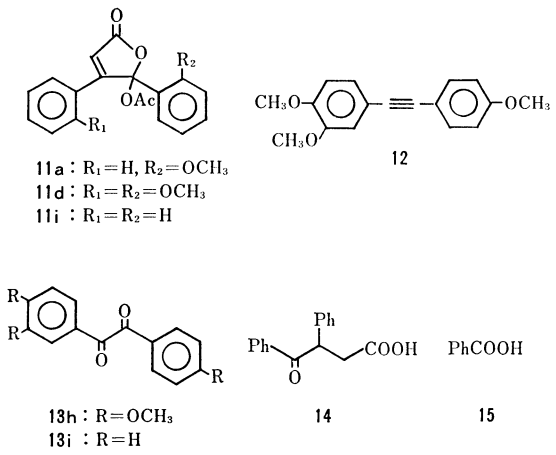
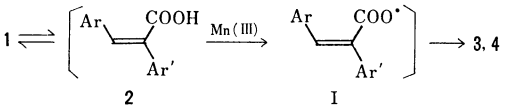
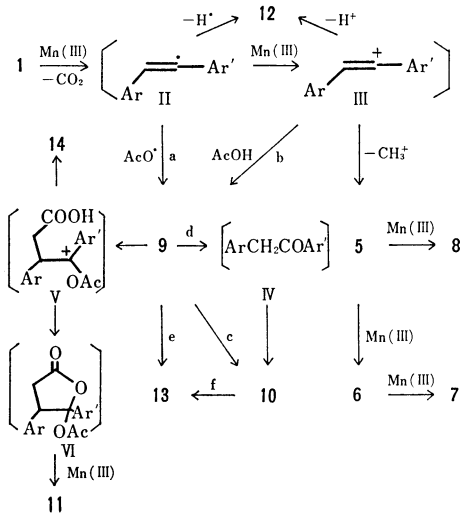


Fig. 1.



Scheme 1.



Scheme 2.

Table 1. Oxidation of α-phenylcinnamic acids with manganese(III) acetate in boiling acetic acid containing acetic anhydride

Entry	Substrate	Reaction conditions: Molar ratio	Reaction conditions: Time/min	Products (yield/%)[a]	Recovered substrate
1	**1a**[20]	1 : 5	18	**5a** (5) **6a** (10) **10a** (7) **11a** (12)	**1a** (43)
2	**1b**[21]	1 : 2	13	**3b** (17) **4b** (14) **5b** (2) **10b** (19)	**1b** (20)
3	**1c**[22]	1 : 2	16	**3c** (10) **3c′** (8)	**1c** (30)
4	**1c**	1 : 4	25	**3c** (4) **3c′** (17)	**1c** (16)
5	**1c**	1 : 5	40	**3c** (3) **3c′** (15)	**1c** (12)
6	**1d**[23]	1 : 5	11	**5d** (5) **6d** (20) **10d** (9) **11d** (12)	**1d** (34)
7	**1e**	1 : 5	12	**3e** (6) **4e** (15) **5e** (2) **6e** (7) **10e** (25)	**1e** (18)
8	**1f**[24]	1 : 2	10	**5f** (34) **6f** (2) **10f** (16)	**1f** (16)
9	**1f**	1 : 5	30	**5f** (15) **6f** (14) **7** (5) **8f** (6) **10f** (32)	**1f** (2)
10	**1g**	1 : 2	6	**5g** (9) **9g** (20) **10g** (21)	**1g** (31)
11	**1h**[25]	1 : 2	3	**3h** (3) **9h** (3) **10h** (25) **12** (9)	**1h** (48)
12	**1h**	1 : 5	8	**3h** (10) **10h** (64) **12** (12)	**1h** (3)

a) The yield is based on the amount of substrate used.

Table 2. Oxidation of (*Z*)-α-acetoxystilbenes (**9**) with manganese(III) acetate

Entry	Substrate	Reaction conditions[a]: Molar ratio of **9** : oxidant	Reaction conditions[a]: Solvent	Reaction conditions[a]: Time/min	Product (yield/%)[b]	Recovered substrate
1	**9h**	1 : 2	AcOH, Ac_2O	2	**10h** (67)	**9h** (22)
2	**9h**	1 : 5	AcOH, Ac_2O	30	**10h** (70) **13h** (6)	
3	**9i**	1 : 3	AcOH, Ac_2O	12	**10i** (13) **11i** (12) **14** (26)	**9i** (34)
4	**9i**	1 : 3	AcOH	95	**10i** (43) **11i** (2) **15** (7)	

a) The reactions were carried out at reflux temperature. b) The yield is based on the amount of the substrate used.

phenyl)-2-(3,4-dimethoxyphenyl)ethanone (**10h**) gives **13h**. In order to establish the true pathway, 2-acetoxy-1,2-diphenylethanone (**10i**) was oxidized with manganese(III) acetate to give **13i** in a 15% yield. The result showed that 3,4,4′-trimethoxybenzil (**13h**) was formed through the f pathway.

The formation of 5-acetoxy-4,5-diphenyl-2(5*H*)-furanones (**11**) from **1** is very interesting, as it may be formed by another reaction of (*Z*)-α-acetoxystilbene (**9**) with manganese(III) acetate. The reaction of (*Z*)-α-acetoxystilbene (**9i**) with manganese(III) acetate did give 5-acetoxy-4,5-diphenyl-2(5*H*)-furanone (**11i**), along with 3,4-diphenyl-4-oxobutanoic acid (**14**) (Table 2, entry 3). The reaction pathway could be explained as follows. The reaction of **9** with the carboxymethyl radical would give a radical. This radical is oxidized to a cation, V, which gives a γ-lactone (VI). The VI would then be oxidized to give **11** via acetoxylation at the 4-position of VI, followed by the elimination of acetic acid. The V cation also reacts with acetic acid and then eliminates acetic anhydride, giving **14** (Scheme 2). It has been mentioned earlier that the yield of **10i** was increased when **9i** was oxidized in acetic acid, but that of **11i** decreased (Table 2, entry 4). This may suggest that diacetoxylation took place[2b] under the present reaction conditions and that the carboxymethyl radicals were produced in smaller amounts. It has previously been reported that the reaction of olefins with manganese(III) acetate under anhydrous conditions gave γ-lactones.[19]

*1-(3,4-Dimethoxyphenyl)-2-(4-methoxyphenyl)acetylene (**12**).* This compound may be formed either from the vinylic radical (II) with a loss of hydrogen or from the vinylic cation (III) with the removal of the proton (Scheme 2).

In conclusion, it was shown that the reactions of (*E*)-α-phenylcinnamic acid (**1**) with manganese (III) acetate could be explained by assuming two radicals, I and II, two cations, III and V, and the lactone VI as the reaction intermediates.

Experimental

All the ^1H NMR spectra were recorded with a Hitachi Perkin-Elmer R-24 spectrometer, with tetramethylsilane as the internal reference. The IR spectra were taken on a JASCO IRA-1 grating spectrometer, while the UV spectra were recorded for the methanol solution with a Hitachi EPS-3T spectrophotometer. The mass spectra were recorded with JMS-01 SG-2 and Hitachi RMU-7M 002CPU mass spectrometers. The melting points were determined with a Yanagimoto micro-melting point apparatus and were not corrected.

*Preparation of α-Phenylcinnamic Acids (**1a—h**).* The general procedure for the preparation of α-phenylcinnamic acids was as follows. A mixture of a benzaldehyde (45 mmol), a phenylacetic acid (36 mmol), triethylamine (30

ml), and acetic anhydride (60 ml) was heated under reflux for 4 h. The reaction mixture was acidified with concd hydrochloric acid (40 ml) and extracted with benzene. This solution was washed with water and then extracted several times with 2 M aqueous sodium hydroxide. The combined extract was then acidified to a pH of 5.9 (the pH adjustment was checked with a Hitachi-Horiba F-5 pH meter) with concd hydrochloric acid. The precipitate was collected by filtration. The crude acid was purified by recrystallization to give (*E*)-α-phenylcinnamic acid. The (*Z*)-isomer was precipitated by the further addition of concd hydrochloric acid to the filtrate. The crude (*Z*)-acid was collected by filtration and recrystallized.

*(E)-2,4-Dimethoxy-α-(2-methoxyphenyl)cinnamic Acid (**1e**)*: Mp 177.5—179 °C (benzene); 20% yield; IR (KBr) 2950 and 1697 cm^{-1} (COOH); UV λ_{max} (log ε) 239^{sh} (4.09), 294 (4.08), and 331 nm (4.23); NMR ($CDCl_3$) δ=3.71 (3H, s, OCH_3), 3.75 (3H, s, OCH_3), 3.81 (3H, s, OCH_3), 6.11 (1H, dd, J=9 and 2.5 Hz, $H_{(5)}$), 6.37 (1H, d, J=2.5 Hz, $H_{(3)}$), 6.74 (1H, d, J=9 Hz, $H_{(6)}$), 6.7—7.5 (4H, m, $H_{(3'-6')}$), 8.24 (1H, s, =CH), and 9.9—11 (1H, br, COOH). Found; C, 68.60; H, 5.82%. Calcd for $C_{18}H_{18}O_5$; C, 68.78; H, 5.77%.

*(Z)-2-Methoxy-α-(4-methoxyphenyl)cinnamic Acid (**2f**)*: Mp 129.5—131 °C (benzene–light petroleum); 0.3% yield; IR (KBr) 2960 and 1705 cm^{-1} (COOH); UV λ_{max} (log ε) 236^{sh} (4.12), 290^{sh} (4.22), and 321 nm (4.25); NMR ($CDCl_3$) δ=3.82 (6H, s, 2×OCH_3), 6.89 (2H, m, $H_{(3')}$ and $H_{(5')}$), 7.46 (2H, m, $H_{(2')}$ and $H_{(6')}$), 6.7—7.6 (4H, m, $H_{(3-6)}$), 7.19 (1H, s, =CH), and 10.57 (1H, br s, COOH). (Found; C, 71.67; H, 5.73%. Calcd for $C_{17}H_{16}O_4$; C, 71.82; H, 5.67%.

*(E)-2,4-Dimethoxy-α-(4-methoxyphenyl)cinnamic Acid (**1g**)*: Mp 217.5—220.5 °C (EtOH); 27% yield; IR (KBr) 2940 and 1680 cm^{-1} (COOH); UV λ_{max} (log ε) 240 (4.17), 295 (4.07), and 336 nm (4.23); NMR (DMSO-d_6) δ=3.72 (3H, s, OCH_3), 3.76 (3H, s, OCH_3), 3.86 (3H, s, OCH_3), 6.20 (1H, dd, J=9 and 2.5 Hz, $H_{(5)}$), 6.54 (1H, d, J=2.5 Hz, $H_{(3)}$), 6.59 (1H, d, J=9 Hz, $H_{(6)}$), 6.90 (2H, m, $H_{(3')}$ and $H_{(5')}$), 7.07 (2H, m, $H_{(2')}$ and $H_{(6')}$), 7.93 (1H, s, =CH), and 11.5 (1H, br, COOH). Found; C, 68.62; H, 5.81%. Calcd for $C_{18}H_{18}O_5$; C, 68.78; H, 5.77%.

*Oxidation of (E)-α-Phenylcinnamic Acids (**1a—h**) with Manganese(III) Acetate.* The general procedure for the oxidation of (*E*)-α-phenylcinnamic acids was as follows. To a hot solution of an (*E*)-α-phenylcinnamic acid (2 mmol) in acetic acid (35 ml) containing acetic anhydride (5 ml), we added manganese(III) acetate dihydrate.[26] The solution was then heated under reflux until the dark color of the Mn-(III) ions disappeared. After the removal of the solvent *in vacuo*, the resulting mixture was triturated with water and extracted with chloroform. The chloroform solution was washed with aqueous sodium carbonate, dried over sodium sulfate, and evaporated under reduced pressure. The products were chromatogrammed on TLC (Wakogel B-10) with chloroform and then ether as developing solvents, and recrystallized. The yields are summarized in Table 1. The aqueous sodium carbonate solution was acidified with concd hydrochloric acid and extracted with ethyl acetate. The ethyl acetate solution was dried and evaporated. The IR spectrum of the resulting substance was superimposible on that of the (*E*)-α-phenylcinnamic acid. The acid was also recovered on TLC. The recovery of the (*E*)-α-phenylcinnamic acid in Table 1 was the sum of them.

*Oxidation Products of **1a**. 2-Phenylbenzofuran (**5a**)*: Mp 120—121 °C (EtOH) (lit,[27] mp 120 °C).

*3-(Acetoxymethyl)-2-phenylbenzofuran (**6a**)*: Liquid; IR ($CHCl_3$) 1750 cm^{-1} (OAc); NMR (CCl_4) δ=2.03 (3H, s, OAc), 5.32 (2H, s, $-CH_2-$), and 6.9—8.0 (9H, m, aromatic). Found; *m/e* 266.0921. Calcd for $C_{17}H_{14}O_3$; M, 266.0943.

*2-Acetoxy-1-phenyl-2-(2-methoxyphenyl) ethanone (**10a**)*: Liquid; IR ($CHCl_3$) 1752 (OAc) and 1715 cm^{-1} (C=O); NMR (CCl_4) δ=2.08 (3H, s, OAc), 3.84 (3H, s, OCH_3), 6.6—7.5 (8H, m, >CH– and aromatic), and 7.7—8.0 (2H, m, $H_{(2)}$ and $H_{(6)}$). Found; *m/e* 284.1041. Calcd for $C_{17}H_{16}O_4$; M, 284.1049.

*5-Acetoxy-4-(2-methoxyphenyl)-5-phenyl-2(5H)-furanone (**11a**)*: Mp 150—152 °C (aq MeOH); IR ($CHCl_3$) 1770 cm^{-1} (α,β-unsaturated γ-lactone[28]); UV λ_{max} (log ε) 236^{sh} (4.03), 283 (4.19), and 334 nm (3.89); NMR ($CDCl_3$) δ=2.12 (3H, s, OAc), 3.89 (3H, s, OCH_3), 6.5—7.9 (9H, m, aromatic), and 7.13 (1H, s, $H_{(3)}$); MS *m/e* 324 (M^+), 282, 265, 254, 237, 177, 132, 105, and 77. Found; C, 70.20; H, 4.96%. Calcd for $C_{19}H_{16}O_5$; C, 70.36; H, 4.98%.

*Oxidation Products of **1b**. 7-Methoxy-3-phenylcoumarin (**3b**)*: Mp 122—123 °C (EtOH) (lit,[29] mp 124 °C).

*8-Methoxy-3-phenyl-1-oxaspiro[4.5]deca-3,7,9-triene-2,6-dione (**4b**)*: Mp 135—137.5 °C (benzene-light petroleum); IR (KBr) 1770 (γ-lactone) and 1675 cm^{-1} (C=O); UV λ_{max} (log ε) 225 (4.38) and 276 nm (4.26); NMR ($CDCl_3$) δ= 3.75 (3H, s, OCH_3), 5.73 (1H, s, $H_{(7)}$), 6.38 (2H, s, $H_{(9)}$ and $H_{(10)}$), 7.25 (1H, s, $H_{(4)}$), 7.3—7.6 (3H, m, $H_{(3'-5')}$), and 7.7—8.1 (2H, m, $H_{(2')}$ and $H_{(6')}$); MS *m/e* 268 (M^+). Found; C, 71.51; H, 4.50%. Calcd for $C_{16}H_{12}O_4$; C, 71.63; H, 4.51%.

*6-Methoxy-2-phenylbenzofuran (**5b**)*: IR and NMR spectra of **5b** separated on TLC were identical with those of an authentic sample.[4]

*2-Acetoxy-1-phenyl-2-(2,4-dimethoxyphenyl)ethanone (**10b**)*: Mp 112—113 °C (benzene–light petroleum); IR (KBr) 1753 (OAc) and 1715 cm^{-1} (C=O); UV λ_{max} (log ε) 239 (4.23), 283 (3.75) and 289^{sh} nm (3.71); NMR ($CDCl_3$) δ=2.18 (3H, s, OAc), 3.77 (3H, s, OCH_3), 3.89 (3H, s, OCH_3), 6.3—6.6 (2H, m, $H_{(3')}$ and $H_{(5')}$), 7.1—7.6 (5H, m, >CH– and aromatic), and 7.8—8.1 (2H, m, $H_{(2)}$ and $H_{(6)}$). Found; C, 68.83; H, 5.86%. Calcd for $C_{18}H_{18}O_5$; C, 68.78; H, 5.77%.

*Oxidation Products of **1c**. 7,8-Dimethoxy-3-phenylcoumarin (**3c**)*: Mp 135.5—136 °C (EtOH) (lit,[30] mp 142—144 °C).

*5,6,7-Trimethoxy-3-phenylcoumarin (**3c'**)*: Mp 143—143.5 °C (MeOH); IR ($CHCl_3$) 1730 cm^{-1} (C=O); UV λ_{max} (log ε) 232^{sh} (4.32), 251^{sh} (4.04), and 351 nm (4.33); NMR ($CDCl_3$) δ=3.85 (3H, s, OCH_3), 3.91 (3H, s, OCH_3), 4.04 (3H, s, OCH_3), 6.64 (1H, s, $H_{(8)}$), 7.2—7.8 (5H, m, Ph), and 8.01 (1H, s, $H_{(4)}$). Found: C, 69.02; H, 5.15%. Calcd for $C_{18}H_{16}O_5$; C, 69.22; H, 5.16%.

*Oxidation Products of **1d**. 2-(2-Methoxyphenyl)benzofuran (**5d**)*: Mp 78.5—80 °C (EtOH) (lit,[31] mp 82—83 °C).

*3-(Acetoxymethyl)-2-(2-methoxyphenyl) benzofuran (**6d**)*: Liquid; IR ($CHCl_3$) 1748 cm^{-1} (OAc); NMR (CCl_4) δ= 1.93 (3H, s, OAc), 3.69 (3H, s, OCH_3), 5.12 (2H, s, $-CH_2-$), and 6.7—7.7 (8H, m, aromatic). Found; *m/e* 296.1059. Calcd for $C_{18}H_{16}O_4$; M, 296.1049.

*2-Acetoxy-1,2-bis(2-methoxyphenyl)ethanone (**10d**)*: Mp 101—102 °C (cyclohexane) (lit,[32] mp 102 °C).

*5-Acetoxy-4,5-bis(2-methoxyphenyl)-2(5H)-furanone (**11d**)*: Mp 143.5—146 °C (MeOH); IR ($CHCl_3$) 1770 cm^{-1} (α,β-unsaturated γ-lactone[28]); UV λ_{max} (log ε) 281 (4.21) and 330 nm (3.89); NMR ($CDCl_3$) δ=2.11 (3H, s, OAc), 3.61 (3H, s, OCH_3), 3.85 (3H, s, OCH_3), 7.06 (1H, s, $H_{(3)}$), 6.6—7.6 (7H, m, aromatic), and 7.79 (1H, dd, J=7.5 and 2 Hz, $H_{(6')}$); MS *m/e* 354 (M^+), 312, 295, 253, 177, 135, 132, 92, 89, and 77. Found; C, 67.81; H, 5.12%. Calcd for $C_{20}H_{18}O_6$; C, 67.79; H, 5.12%.

Oxidation Products of ***1e***. *7-Methoxy-3-(2-methoxyphenyl)-coumarin* (***3e***): Mp 134—135 °C (benzene–light petroleum) (lit,[33] mp 136 °C).

8-Methoxy-3-(2-methoxyphenyl)-1-oxaspiro[4.5]deca-3,7,9-triene-2,6-dione (***4e***): Mp 171—172 °C (CCl_4); IR ($CHCl_3$) 1775 (γ-lactone) and 1680 cm^{-1} (C=O); UV λ_{max} (log ε) 224 (4.40), 240^{sh} (4.30), 277 (4.19), and 311^{sh} nm (3.88); NMR ($CDCl_3$) δ=3.72 (3H, s, OCH_3), 3.89 (3H, s, OCH_3), 5.68 (1H, s, $H_{(7)}$), 6.38 (2H, s, $H_{(9)}$ and $H_{(10)}$), 6.8—7.5 (3H, m, $H_{(3'-5')}$), 7.59 (1H, s, $H_{(4)}$), and 8.40 (1H, dd, J=8 and 2 Hz, $H_{(6')}$); MS *m/e* 298 (M^+). Found; C, 68.25; H, 4.70%. Calcd for $C_{17}H_{14}O_5$; C, 68.45; H, 4.73%.

6-Methoxy-2-(2-methoxyphenyl)benzofuran (***5e***): Mp 87—88 °C (aq EtOH); IR (KBr) 1555, 947, and 910 cm^{-1} (C=C); NMR (CCl_4) δ=3.79 (3H, s, OCH_3), 3.90 (3H, s, OCH_3), 6.5—7.5 (6H, m, aromatic), 7.13 (1H, s, $H_{(3)}$), and 7.96 (1H, dd, J=7.5 and 2.5 Hz, $H_{(6')}$). Found; C, 75.42; H, 5.58%. Calcd for $C_{16}H_{14}O_3$; C, 75.57; H, 5.55%.

3-(Acetoxymethyl)-6-methoxy-2-(2-methoxyphenyl)benzofuran (***6e***): Liquid; IR ($CHCl_3$) 1745 cm^{-1} (OAc); NMR (CCl_4) δ=1.97 (3H, s, OAc), 3.79 (6H, s, 2×OCH_3), 5.10 (2H, s, $-CH_2-$), and 6.6—7.7 (7H, m, aromatic). Found; *m/e* 326.1166. Calcd for $C_{19}H_{18}O_5$; M, 326.1154.

2-Acetoxy-1-(2-methoxyphenyl)-2-(2,4-dimethoxyphenyl)ethanone (***10e***): Mp 111.5—112 °C (ether); IR ($CHCl_3$) 1745 (OAc) and 1698 cm^{-1} (C=O); UV λ_{max} (log ε) 236^{sh} (4.05), 253 (3.94), 288 (3.65), and 313 nm (3.58); NMR ($CDCl_3$) δ=2.14 (3H, s, OAc), 3.67 (3H, s, OCH_3), 3.71 (6H, s, 2×OCH_3), 6.2—6.5 (2H, m, $H_{(3')}$ and $H_{(5')}$), 6.6—7.5 (4H, m, aromatic), 7.14 (1H, s, >CH–), and 7.69 (1H, dd, J=8.5 and 2 Hz, $H_{(6)}$). Found; C, 66.34; H, 5.58%. Calcd for $C_{19}H_{20}O_6$; C, 66.27; H, 5.85%.

Oxidation Products of ***1f***. *2-(4-Methoxyphenyl)benzofuran* (***5f***): Mp 146—147 °C (EtOH) (lit,[4] mp 146 °C).

3-(Acetoxymethyl)-2-(4-methoxyphenyl)benzofuran (***6f***): Mp 72—73 °C (light petroleum); IR ($CHCl_3$) 1740 cm^{-1} (OAc); UV λ_{max} (log ε) 305 nm (4.47); NMR ($CDCl_3$) δ=2.09 (3H, s, OAc), 3.84 (3H, s, OCH_3), 5.38 (2H, s, $-CH_2-$), 6.98 (2H, m, $H_{(3')}$ and $H_{(5')}$), 7.74 (2H, m, $H_{(2')}$ and $H_{(6')}$), and 7.0—7.8 (4H, m, $H_{(4-7)}$). Found: C, 72.85; H, 5.45%. Calcd for $C_{18}H_{16}O_4$; C, 72.96; H, 5.44%.

3-Formyl-2-(4-methoxyphenyl)benzofuran (***7***): Mp 114.5—115.5 °C (cyclohexane); IR ($CHCl_3$) 1678 cm^{-1} (CHO); UV λ_{max} (log ε) 251 (4.28) and 331 nm (4.26); NMR ($CDCl_3$) δ=3.88 (3H, s, OCH_3), 7.08 (2H, m, $H_{(3')}$ and $H_{(5')}$), 7.2—7.7 (3H, m, $H_{(5-7)}$), 7.83 (2H, m, $H_{(2')}$ and $H_{(6')}$), 8.2—8.5 (1H, m, $H_{(4)}$), and 10.25 (1H, s, CHO); MS *m/e* 252 (M^+). Found; C, 76.19; H, 4.84%. Calcd for $C_{16}H_{12}O_3$; C, 76.18; H, 4.80%.

2-Acetoxy-2-(4-methoxyphenyl)-3(2H)-benzofuranone (***8f***): Mp 112.5—113.5 °C (benzene–light petroleum); IR ($CHCl_3$) 1770^{sh} (C=O) and 1747 cm^{-1} (OAc); UV λ_{max} (log ε) 225^{sh} (4.32), 259 (4.11), 283^{sh} (3.58), and 330 nm (3.69); NMR ($CDCl_3$) δ=2.15 (3H, s, OAc), 3.74 (3H, s, OCH_3), 6.83 (2H, m, $H_{(3')}$ and $H_{(5')}$), 7.10 (2H, m, aromatic), 7.48 (2H, m, $H_{(2')}$ and $H_{(6')}$), and 7.3—7.8 (2H, m, aromatic); MS *m/e* 298 (M^+). Found; C, 68.49; H, 4.74%. Calcd for $C_{17}H_{14}O_5$; C, 68.45; H, 4.73%.

2-Acetoxy-1-(4-methoxyphenyl)-2-(2-methoxyphenyl)ethanone (***10f***): Mp 81.5—83.5 °C (hexane); IR ($CHCl_3$) 1745 (OAc) and 1705 cm^{-1} (C=O); UV λ_{max} (log ε) 222 (4.25) and 286 nm (4.27); NMR ($CDCl_3$) δ=2.17 (3H, s, OAc), 3.80 (3H, s, OCH_3), 3.91 (3H, s, OCH_3), 6.83 (2H, m, $H_{(3)}$ and $H_{(5)}$), 6.7—7.5 (4H, m, aromatic), 7.36 (1H, s, >CH–), and 7.97 (2H, m, $H_{(2)}$ and $H_{(6)}$). Found; C, 68.89; H, 5.87%. Calcd for $C_{18}H_{18}O_5$; C, 68.78; H, 5.77%.

Oxidation Products of ***1g***. *6-Methoxy-2-(4-methoxyphenyl)-benzofuran* (***5g***): Mp 156.5—158 °C (EtOH) (lit,[4] mp 159 °C).

(Z)-α-Acetoxy-2',4,4'-trimethoxystilbene (***9g***): Mp 105.5—108.5 °C (benzene–light petroleum); IR ($CHCl_3$) 1762 cm^{-1} (OAc); UV λ_{max} (log ε) 237^{sh} (4.05), 300^{sh} (4.33), and 325 nm (4.41); NMR ($CDCl_3$) δ=2.24 (3H, s, OAc), 3.80 (9H, s, 3×OCH_3), 6.4—6.7 (2H, m, $H_{(3')}$ and $H_{(5')}$), 6.87 (1H, s, =CH), 6.92 (2H, m, $H_{(3)}$ and $H_{(5)}$), 7.48 (2H, m, $H_{(2)}$ and $H_{(6)}$), and 7.56 (1H, m, $H_{(6')}$). Found; C, 69.58; H, 6.27%. Calcd for $C_{19}H_{20}O_5$; C, 69.50; H, 6.14%.

2-Acetoxy-1-(4-methoxyphenyl)-2-(2,4-dimethoxyphenyl)ethanone (***10g***): Liquid; IR ($CHCl_3$) 1750 (OAc) and 1705 cm^{-1} (C=O); NMR ($CDCl_3$) δ=2.16 (3H, s, OAc), 3.74 (3H, s, OCH_3), 3.77 (3H, s, OCH_3), 3.88 (3H, s, OCH_3), 6.2—6.6 (2H, m, $H_{(3')}$ and $H_{(5')}$), 6.81 (2H, m, $H_{(3)}$ and $H_{(5)}$), 7.21 (1H, m, $H_{(6')}$), 7.23 (1H, s, >CH–), and 7.89 (2H, m, $H_{(2)}$ and $H_{(6)}$). Found; *m/e* 344.1235. Calcd for $C_{19}H_{20}O_6$; M, 344.1260.

Oxidation Products of ***1h***. *6,7-Dimethoxy-3-(4-methoxyphenyl)coumarin* (***3h***): Mp 172—173 °C (EtOH); IR ($CHCl_3$) 1730 cm^{-1} (C=O); UV λ_{max} (log ε) 230 (4.42), 249^{sh} (4.15), and 370 nm (4.36); NMR ($CDCl_3$) δ=3.84 (3H, s, OCH_3), 3.92 (3H, s, OCH_3), 3.94 (3H, s, OCH_3), 6.7—7.1 (4H, m, aromatic), 7.67 (2H, m, $H_{(2')}$ and $H_{(6')}$), and 7.68 (1H, s, $H_{(4)}$). Found; C, 69.10; H, 5.26%. Calcd for $C_{18}H_{16}O_5$; C, 69.22; H, 5.16%.

(Z)-α-Acetoxy-3',4,4'-trimethoxystilbene (***9h***): Mp 108.5—109 °C (benzene–light petroleum); IR ($CHCl_3$) 1760 cm^{-1} (OAc); UV λ_{max} (log ε) 320 nm (4.48); NMR ($CDCl_3$) δ=2.28 (3H, s, OAc), 3.82 (3H, s, OCH_3), 3.89 (6H, s, 2×OCH_3), 6.52 (1H, s, =CH–), 6.88 (2H, m, $H_{(3)}$ and $H_{(5)}$), 6.7—7.2 (3H, m, $H_{(2')}$, $H_{(5')}$, and $H_{(6')}$), and 7.46 (2H, m, $H_{(2)}$ and $H_{(6)}$). Found; C, 69.21; H, 6.20%. Calcd for $C_{19}H_{20}O_5$; C, 69.50; H, 6.14%.

2-Acetoxy-1-(4-methoxyphenyl)-2-(3,4-dimethoxyphenyl)ethanone (***10h***): Liquid; IR ($CHCl_3$) 1750 (OAc) and 1705 cm^{-1} (C=O); NMR (CCl_4) δ=2.07 (3H, s, OAc), 3.66 (6H, s, 2×OCH_3), 3.69 (3H, s, OCH_3), 6.68 (2H, m, $H_{(3)}$ and $H_{(5)}$), 6.5—7.0 (4H, m, >CH– and aromatic), and 7.77 (2H, m, $H_{(2)}$ and $H_{(6)}$). Found; *m/e* 344.1238. Calcd for $C_{19}H_{20}O_6$; M, 344.1260.

1-(3,4-Dimethoxyphenyl)-2-(4-methoxyphenyl)acetylene (***12***): Mp 107—107.5 °C (EtOH); IR ($CHCl_3$) 2840 cm^{-1} (OCH_3); UV λ_{max} (log ε) 247^{sh} (4.04), 298 (4.49), 310 (4.46), and 319 nm (4.46); NMR ($CDCl_3$) δ=3.78 (3H, s, OCH_3), 3.86 (6H, s, 2×OCH_3), 6.83 (2H, m, $H_{(3')}$ and $H_{(5')}$), 6.7—7.3 (3H, m, $H_{(2)}$, $H_{(5)}$, and $H_{(6)}$), and 7.41 (2H, m, $H_{(2')}$ and $H_{(6')}$); MS *m/e* 268 (M^+). Found; C, 75.90; H, 6.12%. Calcd for $C_{17}H_{16}O_3$; C, 76.10; H, 6.01%.

Oxidation of 2-Phenylbenzofuran (***5a***). A mixture of 2-phenylbenzofuran (**5a**)[27] (194 mg), manganese(III) acetate dihydrate (2.68 g), acetic acid (30 ml), and acetic anhydride (2 ml) was heated under reflux for 2.5 h. After the removal of the acetic acid *in vacuo*, the resulting mixture was triturated with chloroform and filtered. The filtrate was concentrated and separated on TLC, giving **5a** (25 mg), 3-(acetoxymethyl)-2-phenylbenzofuran (**6a**) (86.7 mg, 30%), and 2-acetoxy-2-phenyl-3(2*H*)-furanone (**8a**) (67.7 mg, 25%); mp 128—129 °C (light petroleum); IR ($CHCl_3$) 1770 (C=O) and 1748 cm^{-1} (OAc); UV λ_{max} (log ε) 257 (4.11) and 329 nm (3.55); NMR ($CDCl_3$) δ=2.14 (3H, s, OAc) and 6.9—7.8 (9H, m, aromatic) (Found: C, 71.80; H, 4.41%. Calcd for $C_{16}H_{12}O_4$; C, 71.63; H, 4.51%).

Preparation of (Z)-α-Acetoxy-3',4,4'-trimethoxystilibene (***9h***). A mixture of 3,4-dimethoxybenzyl 4-methoxyphenyl ketone[34] (1.8 g), freshly fused potassium acetate (3.6 g), and acetic anhydride (60 ml) was heated under reflux for 5 h. After

the removal of the acetic anhydride *in vacuo*, the residue was extracted with chloroform. The chloroform solution was washed with aqueous sodium hydrogencarbonate, dried, and evaporated. The crude product was purified on TLC, using chloroform as the developing solvent, and by recrystallization, giving colorless needles (900 mg, 44%), mp 108.5—109 °C (MeOH).

*Oxidation of (Z)-α-Acetoxystilbene (**9**).* The general procedure for the oxidation of (*Z*)-α-acetoxystilbene (**9**) was as follows. A mixture of **9** (1 mmol), manganese(III) acetate dihydrate (2—5 mmol), and a solvent (20 ml) was heated under reflux for the time shown in Table 2. After being worked-up in a manner similar to that used in the oxidation of (*E*)-α-phenylcinnamic acids (**1**), the following products were obtained (the yields are summarized in Table 2): (*Z*)-α-Acetoxy-3′,4,4′-trimethoxystilbene (**9h**) gave **10h** and 3,4,4′-trimethoxybenzil (**13h**); mp 123—124 °C (EtOH); IR ($CHCl_3$) 1670 cm^{-1} (C=O); UV λ_{max} (log ε) 228 (4.29), 295 (4.36), and 322^{sh} nm (4.23); NMR ($CDCl_3$) δ=3.87 (3H, s, OCH_3), 3.93 (6H, s, 2×OCH_3), 6.89 (1H, d, J=7.5 Hz, $H_{(5)}$), 6.95 (2H, m, $H_{(3')}$ and $H_{(5')}$), 7.3—7.6 (2H, m, $H_{(2)}$ and $H_{(6)}$), and 7.92 (2H, m, $H_{(2')}$ and $H_{(6')}$) (Found; C, 68.05; H, 5.48%. Calcd for $C_{17}H_{16}O_5$; C, 67.99; H, 5.37%). (*Z*)-α-Acetoxystilbene (**9i**)[35] yielded 2-acetoxy-1,2-diphenylethanone (**10i**); mp 81.5—82.5 °C (benzene–hexane) (lit,[36] mp 83 °C); 5-acetoxy-4,5-diphenyl-2(5*H*)-furanone (**11i**); liquid; IR ($CHCl_3$) 1770 cm^{-1}; NMR ($CDCl_3$) δ=2.16 (3H, s, OAc), 6.61 (1H, s, $H_{(3)}$), and 7.2—7.7 (10H, m, 2×Ph); MS *m/e* 294 (M^+), 252, 235, 147, 105, 102, and 77, and 3,4-diphenyl-4-oxobutanoic acid (**14**); mp 148—149 °C (benzene–light petroleum) (lit,[37] mp 161 °C); IR ($CHCl_3$) 1705 (C=O), 1735 (COOH), and 2400—3600 cm^{-1} (COOH); NMR ($CDCl_3$) δ=2.72 (1H, dd, J=18 and 6 Hz, -CH-), 3.41 (1H, dd, J=18 and 9 Hz, -CH-), 5.05 (1H, dd, J=9 and 6 Hz, >CH-), 7.0—7.6 (8H, m, aromatic), 7.90 (2H, m, aromatic), and 9.95 (1H, br, s, COOH), and benzoic acid (**15**).

*Oxidation of 2-Acetoxy-1,2-diphenylethanone (**10h**).* A mixture of **10h** (254 mg), manganese(III) acetate dihydrate (536 mg), acetic acid (20 ml), and acetic anhydride (0.4 ml) was heated under reflux for 3 h. After the removal of the solvent, the resulting mixture was extracted with chloroform. The chloroform solution was concentrated and the resulting substance was chromatogrammed on TLC by developing with chloroform, giving **13i** (31 mg, 15%) and unchanged **10i** (173 mg, 68%).

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