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The Facile Synthesis of Dihydrofurans by the Oxidation of Olefins with Tris(2,4-pentanedionato)manganese(III)

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Eleven olefins were oxidized with tris(2,4-pentanedionato)manganese(III) at the reflux temperature to give the corresponding 3-acetyl-2-methyl-4,5-dihydrofurans in good yields. The oxidation of 9-benzylidene-9,10-dihydroanthracene under the same reaction conditions did not produce the corresponding dihydrofuran, but 9-[α-(1-acetyl-2-hydroxy-1-propenyl)benzylidene]-9,10-dihydroanthracene. When 1,1-diphenylethene was oxidized at room temperature, 3-acetyl-2-hydroperoxy-2-methyl-5,5-diphenyltetrahydrofuran was obtained in a high yield. The effects of the solvent and the additives on the yield of dihydrofuran, the comparable reactivities of other (2,4-pentanedionato)metal complexes, such as Co(III), Cr(III), Fe(III), and Cu(II), and the reaction mechanism are discussed.

In previous papers it was reported that the reaction of malonic acid with olefins in the presence of manganese(III) acetate, $\mathrm{Mn(OAc)_3}$, gave spirobi-γ-lactones,[1] while a similar reaction of malonamide yielded 2-buten-4-olides and/or 1*H*-pyrrol-2(5*H*)-ones.[2] The formation of these lactones and lactams can be explained by a proposed mechanism based on the generation of radicals from malonic acid and malonamide.[2] The reactions of β-dicarbonyl compound with olefins in the presence of $\mathrm{Tl(OAc)_3}$,[3] $\mathrm{Pb(OAc)_4}$,[4] $\mathrm{Mn(OAc)_3}$,[5] AgO, and $\mathrm{PbO_2}$[6] have also been reported to give dihydrofurans. The yields of dihydrofurans, however, were not always satisfactory, and it seems possible to improve the yields by using tris(2,4-pentanedionato)manganese(III), $\mathrm{Mn(acac)_3}$, in a donor solvent such as acetic acid, which can complex manganese(III) ions. This is because Mn(III) complexes generally tend to undergo a rapid exchange of ligands (ligand-exchange reaction),[7] and hence $\mathrm{Mn(acac)_3}$ will be easily decomposed in the donor solvent to form $\cdot\mathrm{CH(COCH_3)_2}$ radicals directly. This radical should react with olefins in the reaction mixture to produce the corresponding dihydrofurans. The present author was interested in this active property of Mn(III) complexes and investigated the title reaction. It is known in general that $\mathrm{Mn(acac)_3}$ can be used as a catalyst in a polymerization reaction[8] and as one-electron-transfer oxidant in coupling reactions of phenols[9] or thiophenols.[10]

Results and Discussion

When 1,1-diphenylethene (**1a**) was oxidized with $\mathrm{Mn(acac)_3}$ in acetic acid at the reflux temperature, it gave 3-acetyl-2-methyl-5,5-diphenyl-4,5-dihydrofuran (**2a**), together with a small amount of benzophenone (**3a**). The reaction was repeated in various solvents, but it was found that acetic acid was the best of all, as is shown in Table 1. The effects of various additives were then examined. The addition of acetic anhydride to the reaction mixture decreased the yield of **2a**, but the reaction time was shortened considerably (Table 2, Entry 2). When β-dicarbonyl compounds were added to the reaction mixture, they still gave **2a** predominantly, thus proving that $\mathrm{Mn(acac)_3}$ is a more active species than the $\cdot\mathrm{CH(CO_2H)_2}$, $\cdot\mathrm{CH(CONH_2)_2}$, and $\cdot\mathrm{CH(CO_2Et)_2}$ radicals (Table 2, Entries 3—5).[1,2]

When **1a** was oxidized with $\mathrm{Mn(acac)_3}$ at room temperature for 12 h, **2a** (6%) and 3-acetyl-2-hydroperoxy-2-methyl-5,5-diphenyltetrahydrofuran (**8**; 89%) were isolated from the reaction mixture. The structure of **8** was determined on the basis of its spectral data. The treatment of **8** with acetic anhydride gave the corresponding (acetyldioxy)tetrahydrofuran **9**. The same oxidation under a nitrogen atmosphere

Table 1. Oxidation of 1,1-diphenylethene (**1a**) with $\mathrm{Mn(acac)_3}$ in various solvents[a,b]

Entry	Solvent	Reaction time	Recovery	Product/yield/%[c]	
		h	%	**2a**	**3a**
1	Acetic acid	2.5[d]	3	89	2
2	Propionic acid	1[d]	35	60	5
3	Acetylacetone	1	32	53	
4	Acetone	24	38	18	23
5	Methanol	24	30	15	24
6	DMSO	24	18		12
7	Benzene	24	53	16	15

a) The reaction was carried out at the reflux temperature. b) **1a** (1 mmol) and $\mathrm{Mn(acac)_3}$ (2 mmol) were employed. c) The yields are based on the amount of **1a** used. d) Minutes.

Table 2. Oxidation of 1,1-diphenylethene (**1a**) with $Mn(acac)_3$ in the presence of some additives in boiling acetic acid

Entry	Additive	Molar ratio of **1a**: additive: $Mn(acac)_3$	Time s	Recovery %	Product/yield/%[a) **2a**	**12**[b)]	**13**[c)]
1	None	1 : 0 : 2	150	3	89		
2	Ac_2O	1 : 20 : 2	10	17	73		
3	$CH_2(CO_2H)_2$	1 : 1 : 2	10	14	75	2	
4	$CH_2(CONH_2)_2$	1 : 4 : 2	10	22	50		9
5	$CH_2(CO_2Et)_2$	1 : 4 : 2	10	9	90		

a) The yields are based on the **1a** used. b) 3,3,8,8-Tetraphenyl-2,7-dioxaspiro[4.4]nonane-1,6-dione.[1) c) 2-Carbamoyl-4,4-diphenyl-2-buten-4-olide.[2)

for 27 h yielded **2a** (27%) and **8** (67%).

Similar reactions of **1a** were carried out by using $Co(acac)_3$, $Cr(acac)_3$, $Fe(acac)_3$, and $Cu(acac)_2$ instead of $Mn(acac)_3$. In the case of $Co(acac)_3$, the reaction gave **2a** (66%), but the reaction took more than 1 h. The reaction with the other oxidants did not occur in boiling acetic acid. It seems that these complexes are stable under the present reaction conditions.

The reactions of 1,1-bis(4-methoxyphenyl)ethene (**1b**), 2-phenylpropene (**1c**), styrene (**1d**), acenaphthylene (**1e**), 1,1,2-triphenylethene (**1f**), 1,1-bis(4-methoxyphenyl)-2-phenylethene (**1g**), 1,1,2-tris(4-methoxyphenyl)ethene (**1h**), 9-benzylidene-9*H*-xanthene (**1i**), 9-benzylidene-9,10-dihydroanthracene (**1j**), and 1-heptene (**1k**) with $Mn(acac)_3$ were also carried out in acetic acid to yield the corresponding dihydrofurans **2b—i** and **2k**, except for **1j** (Fig. 1 and Table 3). In the cases of **1g** and **1h**, acetoxyethenes **4g** and **4h** were mainly produced rather than the dihydrofurans **2g** and **2h**. For the reaction of **1j** with $Mn(acac)_3$, the corresponding dihydrofuran was not isolated, but 9-[α-(1-acetyl-2-hydroxy-1-propenyl)benzylidene]-9,10-dihydroanthracene (**7j**) was obtained. The dienone **7j** was heated with $Mn(OAc)_3$ in acetic acid in the hope obtaining the corresponding dihydrofuran.[11) However, this was not formed, and the products were found to be **10** and **11** (Scheme 1). The absorption bands at 395, 374, 355, and 338 nm in the UV spectrum of **10** are similar to those of anthracene, and the ^{1}H-NMR and the IR spectrum showed that a 1-acetyl-2-hydroxy-1-propenyl group remained intact. Thus, the structure of **10** was determined to be 9-(1-acetoxy-2-acetyl-3-hydroxy-1-phenyl-2-butenyl) anthracene. The ^{13}C-NMR spectrum of **11** (R=Ac) indicated the structure of 9-acetoxy-9-(2-acetyl-3-oxo-1-phenyl-1-butenyl)-9,10-dihydroanthracene.

The mechanism for the formation of the dihydrofurans can be depicted as involving the α,α′-diketo radical, which is generated directly by the thermolysis of $Mn(acac)_3$ (Scheme 2).[5) It appears that acetic acid as a donor solvent facilitates the ligand-exchange reaction of $Mn(acac)_3$, while the addition of acetic

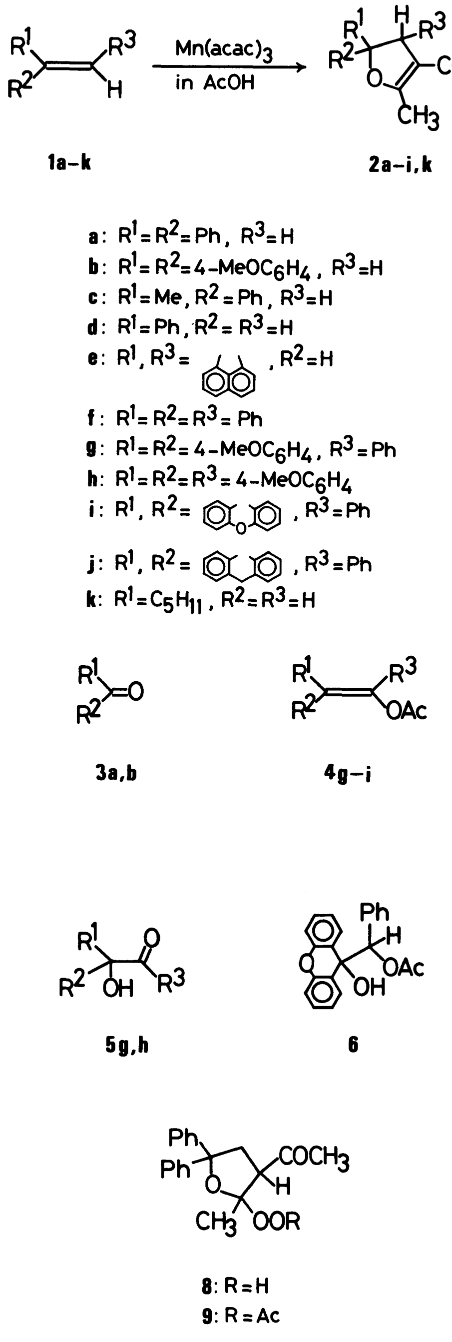
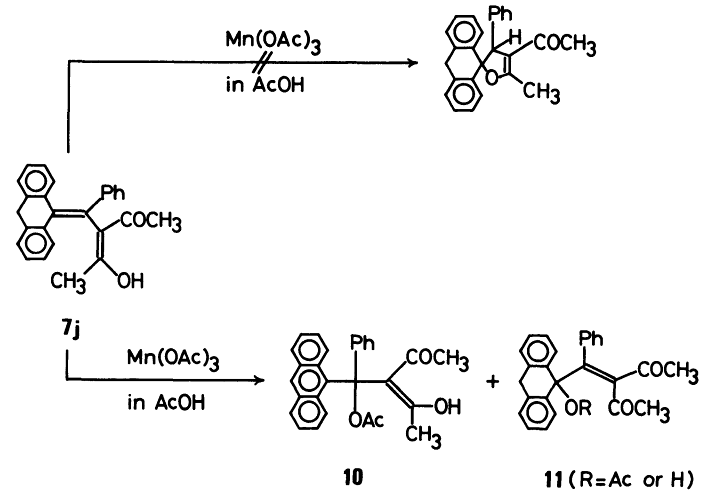


Fig. 1.

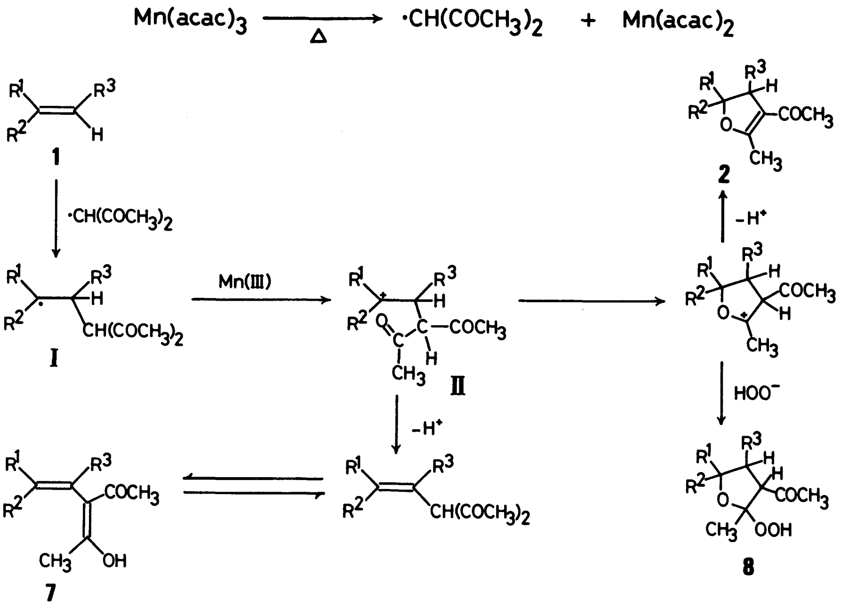
Table 3. Oxidation of olefins with $Mn(acac)_3$ in boiling acetic acid

Entry	Substrate	Molar ratio of **1**: $Mn(acac)_3$	Time / min	Recovery / %	Product/yield/%[a)					
1	**1a**	1 : 2	2.5	3	**2a** (89)	**3a** (2)				
2	**1b**	1 : 2	1	5	**2b** (88)	**3b** (5)				
3	**1c**	1 : 2	3		**2c** (97)					
4	**1d**	1 : 2	3		**2d** (75)					
5	**1e**	1 : 3	5	4	**2e** (70)					
6	**1f**	1 : 6	3	57	**2f** (41)					
7	**1g**	1 : 4	3	2	**2g** (29)		**4g** (56)	**5g** (5)		
8	**1h**	1 : 4	3		**2h** (13)		**4h** (57)	**5h** (14)		
9	**1i**	1 : 4	3	3	**2i** (44)		**4i** (21)		**6** (23)	
10	**1j**	1 : 2	3							**7j** (70)
11	**1k**	1 : 2	3		**2k** (12)					

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



Scheme 1.



Scheme 2.

anhydride or β-dicarbonyl compounds accelerates the thermolysis of Mn(acac)$_3$, as in the oxidation of olefins with Mn(OAc)$_3$ in the presence of acetic anhydride.[12] The reason for the failure to cyclize **7j** to the corresponding dihydrofuran is not evident. However, it could be pointed out that the cyclization may occur at the stage of the carbonium ion **II** and that one of the oxygen functions and the C-1 in **7j** are too far apart to ring-closure.

The reaction of olefins with acetylacetone in the presence of Mn(OAc)$_3$ by the method of Heiba and Dessau[5] gave dihydrofurans in similar yields. In their method, an excess of acetylacetone was needed, and the reaction took more than 10 min. In the present author's method, however, only a stoichiometrical amount of Mn(acac)$_3$ was required for the synthesis of dihydrofurans, except in the case of trisubstituted olefins **1f—i**. Moreover, the oxidation with Mn(acac)$_3$ was completed within 3 min.

The reaction of Mn(acac)$_3$ with olefins is most successful when ethenes containing an aryl group are used. This is primarily due to the electronic effect of the aryl group, which could stabilize the intermediate radical **I** and the cation **II**. Alkyl-substituted olefin **1k** gave the lowest yield. The yields of dihydrofurans from trisubstituted olefins **1f—i** range from moderate to poor. It should be pointed out that the furans are always formed by the attack of the α,α'-diketo radical on the less substituted carbon in ethenes. This is probably attributable to steric reasons.

Thus, it has been shown that the reaction of Mn(acac)$_3$ with aryl-substituted olefins is a useful method for the preparation of substituted dihydrofurans.

Experimental

Measurements. The melting points are uncorrected. The IR spectra were taken on a JASCO A-102 infrared spectrometer, and the IR spectral data are expressed in cm^{-1}. The ^{1}H- and ^{13}C-NMR spectra were recorded on a Hitachi Perkin-Elmer R-24 spectrometer and a JEOL FX-100 spectrometer at room temperature. The chemical shifts are recorded in the δ scale, relative to TMS as an internal standard. The mass spectra were obtained with a JEOL JMS-DX-300 mass spectrometer using a direct-insertion probe at an ionizing voltage of 70 eV. The UV spectrum is measured on a Hitachi 220A spectrophotometer in a methanol solution.

Materials. The Mn(acac)$_3$ and olefins (**1a—c**, **f—j**) were prepared according to the method described in the literature.[2,13] The Co(acac)$_3$, Cr(acac)$_3$, Fe(acac)$_3$, Cu(acac)$_2$, and olefins (**1d**, **e**, and **k**) were obtained from commercial samples of the Wako Pure Chemical Industries, Ltd.

Oxidation of Olefins with Mn(acac)$_3$. A typical procedure for the oxidation of olefins with Mn(acac)$_3$ was as follows. To a heated solution of olefin (1 mmol) in acetic acid (25 cm^3), the amount of Mn(acac)$_3$ shown in Table 3 was added. The solution was then heated under reflux until the brown color of the Mn(III) ion disappeared (within 3 min). The solvent was removed *in vacuo*, and the residue was triturated with 2 M (1 M=1 mol dm^{-3}) hydrochloric acid and then extracted with chloroform. The products were separated on TLC (Kieselgel 60G), with chloroform as the developing solvent. The yields are summarized in Table 3.

Oxidation Products. *3-Acetyl-2-methyl-5,5-diphenyl-4,5-dihydrofuran (**2a**)*: Yellow liquid; bp 180—185 °C/133 Pa (bath temperature); IR (CHCl$_3$) 1667 (C=O) and 1620 (C=C); ^{1}H-NMR (CDCl$_3$) δ=2.13 (3H, s, COCH$_3$), 2.32 (3H, t, J=1.2 Hz, CH$_3$), 3.61 (2H, q, J=1.2 Hz, CH$_2$), and 7.13—7.50 (10H, m, ArH). Found: m/z 278.12918. Calcd for $C_{19}H_{18}O_2$: M, 278.13068.

*3-Acetyl-5,5-bis(4-methoxyphenyl)-2-methyl-4,5-dihydrofuran (**2b**)*: Colorless needles (from benzene/light petroleum); mp 96.0—96.5 °C; IR (CHCl$_3$) 1664 (C=O); ^{1}H-NMR (CDCl$_3$) δ=2.28 (3H, s, COCH$_3$), 2.30 (3H, t, J=1.2 Hz, CH$_3$), 3.55 (2H, q, J=1.2 Hz, CH$_2$), 3.73 (6H, s, 2×OCH$_3$), and 6.69—7.27 (8H, m, ArH). Found: C, 74.24; H, 6.49%. Calcd for $C_{21}H_{22}O_4$: C, 74.55; H, 6.55%.

In the oxidation of **1a** and **1b**, small amounts of benzophenone (**3a**) and 4,4′-dimethoxybenzophenone (**3b**) were also obtained.

*3-Acetyl-2,5-dimethyl-5-phenyl-4,5-dihydrofuran (**2c**)*: Yellow liquid; bp 160—165 °C/133 Pa (bath temperature).[6]

*3-Acetyl-2-methyl-5-phenyl-4,5-dihydrofuran (**2d**)*: Yellow liquid; bp 140 °C/133 Pa (bath temperature).[4]

*7-Acetyl-8-methyl-*cis*-6b,9a-dihydroacenaphtho[1,2-*b*]furan (**2e**)*: Pale orange needles (from benzene/hexane); mp 149.7—150.2 °C; IR (CHCl$_3$) 1660 (C=O) and 1622 (C=C); ^{1}H-NMR (CDCl$_3$) δ=2.07 (3H, d, J=1.2 Hz, CH$_3$), 2.26 (3H, s, COCH$_3$), 5.12 (1H, br. d, J=7.8 Hz, H-6b), 6.20 (1H, d, J=7.8 Hz, H-9a), and 7.15—7.80 (6H, m, ArH). Found: C, 81.35; H, 5.67%. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64%.

*3-Acetyl-2-methyl-4,5,5-triphenyl-4,5-dihydrofuran (**2f**)*: Colorless microcrystals (from benzene/light petroleum); mp 139.5—140.5 °C; IR (CHCl$_3$) 1665 (C=O) and 1622 (C=C); ^{1}H-NMR (CCl$_4$) δ=1.80 (3H, s, COCH$_3$), 2.40 (3H, d, J=1.2 Hz, CH$_3$), 4.98 (1H, q, J=1.2 Hz, >CH-), and 6.70—7.69 (15H, m, ArH). Found: C, 84.65; H, 6.33%. Calcd for $C_{25}H_{22}O_2$: C, 84.71; H, 6.26%.

*Oxidation Products of **1g**.* *3-Acetyl-5,5-bis(4-methoxyphenyl)-2-methyl-4-phenyl-4,5-dihydrofuran (**2g**)*: Colorless liquid; IR (CHCl$_3$) 1664 (C=O); ^{1}H-NMR (CDCl$_3$) δ=1.89 (3H, s, COCH$_3$), 2.42 (3H, d, J=1.2 Hz, CH$_3$), 3.47 (3H, s, OCH$_3$), 3.66 (3H, s, OCH$_3$), 4.97 (1H, q, J=1.2 Hz, >CH-), and 6.36—7.60 (13H, m, ArH). Found: m/z 414.18228. Calcd for $C_{27}H_{26}O_4$: M, 414.18311.

*1-Acetoxy-2,2-bis(4-methoxyphenyl)-1-phenylethene (**4g**)*: Colorless microcrystals (from ethanol); mp 103.0—103.5 °C (lit,[2] mp 101—102 °C).

*2-Hydroxy-2,2-bis(4-methoxyphenyl)-1-phenylethanone (**5g**)*: The ^{1}H-NMR and IR spectral data were in agreement with those of an authentic sample.[2]

*Oxidation Products of **1h**.* *3-Acetyl-4,5,5-tris(4-methoxyphenyl)-2-methyl-4,5-dihydrofuran (**2h**)*: Colorless liquid; IR (CHCl$_3$) 1664 (C=O); ^{1}H-NMR (CDCl$_3$) δ=1.90 (3H, s, COCH$_3$), 2.45 (3H, d, J=1.2 Hz, CH$_3$), 3.57 (3H, s, OCH$_3$), 3.61 (3H, s, OCH$_3$), 3.73 (3H, s, OCH$_3$), 4.94 1H, q, J=1.2 Hz, >CH-), and 6.41—7.55 (12H, m, ArH).

Found: m/z 444.19165. Calcd for $C_{28}H_{28}O_5$: M, 444.19368.

1-Acetoxy-1,2,2-tris(4-methoxyphenyl)ethene (4h) and 2-Hydroxy-1,2,2-tris(4-methoxyphenyl)-1-ethanone (5h): These ^1H-NMR and IR spectral data were compatible with those of authentic samples.[2]

Oxidation Products of 1i. *4-Acetyl-5-methyl-3-phenylspiro[furan-2(3H), 9′-xanthene] (2i)*: Colorless prisms (from aqueous ethanol); mp 141 °C; IR ($CHCl_3$) 1665 (C=O); ^1H-NMR ($CDCl_3$) δ=1.74 (3H, s, $COCH_3$), 2.68 (3H, d, J=1.2 Hz, CH_3), 4.44 (1H, q, J=1.2 Hz, >CH-), and 6.57—7.57 (13H, m, ArH). Found: C, 81.56; H, 5.59%. Calcd for $C_{25}H_{20}O_3$: C, 81.50; H, 5.47%.

9-(α-Acetoxybenzylidene)-9H-xanthene (4i): Colorless plates (from ethanol); mp 156—157 °C; IR ($CHCl_3$) 1758 (OAc); ^1H-NMR ($CDCl_3$) δ=2.04 (3H, s, OAc) and 6.49—8.00 (13H, m, ArH). Found: C, 80.26; H, 4.95%. Calcd for $C_{22}H_{16}O_3$: C, 80.47; H, 4.91%.

9-(α-Acetoxybenzyl)-9-xanthenol (6): The ^1H-NMR and IR spectra were identical with those of an authentic sample.[2]

Oxidation Product of 1j. *9-[α-(1-Acetyl-2-hydroxy-1-propenyl)benzylidene]-9,10-dihydroanthracene (7j)*: Colorless microcrystals (from ethanol); mp 181.3—181.8 °C; IR ($CHCl_3$) 3600—3200 (OH) and 1600 (C=O); ^1H-NMR ($CDCl_3$) δ=1.64 (6H, s, $2\times CH_3$), 5.09 (2H, s, CH_2), 7.20 (5H, s, Ph), 7.40—8.38 (8H, m, ArH), and 17.02 (1H, s, OH). Found: C, 85.09; H, 6.12%. Calcd for $C_{26}H_{22}O_2$: C, 85.21; H, 6.05%.

Oxidation of **1a** *with Mn(acac)₃ in the Presence of Additives.* To a heated solution of **1a** and an additive in acetic acid (25 cm^3), Mn(acac)$_3$ was added (see Table 2). The mixture was then heated under reflux and worked-up according to the procedure previously described.

When malonic acid was used in the reaction mixture, 3,3,8,8-tetraphenyl-2,7-dioxaspiro[4.4]nonane-1,6-dione (**12**)[1] was formed as a by-product. The reaction using malonamide gave **2a**, together with 2-carbamoyl-4,4-diphenyl-2-buten-4-olide (**13**).[2]

Oxidation of **1a** *with Mn(acac)₃ at Room Temperature.* The olefin **1a** (1 mmol) and Mn(acac)$_3$ (2 mmol) were stirred in acetic acid (25 cm^3) at room temperature for 12 h. The subsequent treatment of the reaction mixture by the above method yielded **2a** (6%) and **8** (89%).

3-Acetyl-2-hydroperoxy-2-methyl-5,5-diphenyltetrahydrofuran (8): Colorless prisms (from ethanol); mp 161—162 °C; IR ($CHCl_3$) 3600—3200 (OH) and 1696 (C=O); ^1H-NMR ($CDCl_3$) δ=1.26 (3H, s, CH_3), 2.28 (3H, s, $COCH_3$), 2.81 (3H, m, $-CH_2-CH<$), 4.20 (1H, s, OH), 7.28 (5H, s, Ph), and 7.26—7.70 (5H, m, Ph); ^{13}C-NMR ($CDCl_3$) δ=209.244 (s, C=O), 143.047 (s, ArC), 140.520 (s, ArC), 128.515 (d, ArC), 128.308 (d, ArC), 128.017 (d, ArC), 127.401 (d, ArC), 126.697 (d, ArC), 125.814 (d, ArC), 98.131 (s, C-2), 85.158 (s, C-5), 52.487 (d, C-3), 32.143 (t, C-4), 29.736 (q, $CO\underline{C}H_3$), and 24.687 (q, CH_3); MS m/z (rel intensity), 312 (M$^+$, 1), 279 (65), 182 (60), 105 (100), 77 (100), and 43 (100). Found: C, 72.93; H, 6.39%. Calcd for $C_{19}H_{20}O_4$: C, 73.06; H, 6.45%.

Reaction of **8** *with Acetic Anhydride.* The product **8** (101.4 mg) was heated under reflux in acetic anhydride (20 cm^3) for 4 h. The solvent was then removed under reduced pressure, and the residue was triturated with 2 M HCl (20 cm^3). The aqueous solution was extracted with chloroform, and the products were separated on TLC.

2-Acetyldioxy-3-acetyl-2-methyl-5,5-diphenyltetrahydrofuran (9): 57.7 mg, 50%; colorless needles (from ethanol); mp 117.5—118.0 °C; IR ($CHCl_3$) 1754 (OAc) and 1701 ($COCH_3$); ^1H-NMR ($CDCl_3$) δ=1.70 (3H, s, CH_3), 2.11 (3H, s, OAc), 2.25 (3H, s, $COCH_3$), 2.73—3.06 (3H, m, $-CH_2-CH<$), 7.22 (5H, s, Ph), and 7.15—7.65 (5H, m, Ph); MS m/z (rel intensity), 354 (M$^+$, 10), 279 (73), 180 (100), 105 (100), and 43 (100). Found: C, 71.00; H, 6.31%. Calcd for $C_{21}H_{22}O_5$: C, 71.17; H, 6.26%.

Oxidation of **1a** *with (2,4-Pentanedionato) Metal Complexes.* The olefin **1a** (1 mmol) and Co(acac)$_3$ (2 mmol) were heated under reflux in acetic acid (25 cm^3) until the dark green color of the Co(III) ion turned to the pink color of the Co(II) ion (for 1 h). The change in the color of the reaction mixture was monitored by means of TLC. The mixture was then treated by the procedure described above, and **1a** (13% recovered) and **2a** (66%) were obtained. The reaction of **1a** (1 mmol) with Cr(acac)$_3$, Fe(acac)$_3$, and Cu(acac)$_2$, respectively (2 mmol of each), under reflux for 4 h in acetic acid, did not give **2a** (**1a** was recovered in 92, 89, and 85% yields, respectively).

The Attempt of Cyclization of **7j** *with Mn (OAc)₃.* The **7j** compound (0.5 mmol) was oxidized with Mn(OAc)$_3$ (2 mmol) in acetic acid (25 cm^3). The mixture was heated under reflux for 10 min and then treated by the above method. However, the cyclization reaction did not occur (**7j** was recovered in a 3%-yield), and **10** and **11** were obtained instead of the corresponding dihydrofuran.

9-(1-Acetoxy-2-acetyl-3-hydroxy-1-phenyl-2-butenyl)anthracene (10): 45%; colorless microcrystals (from benzene/ethanol); mp 245.5—246.5 °C; UV(MeOH) λ_{max}nm (log ε), 338 (3.59), 355 (3.89), 374 (4.10), and 395 (4.12); IR ($CHCl_3$) 3600—3200 (OH), 1728 (OAc), and 1600 (C=O); ^1H-NMR ($CDCl_3$) δ=1.64 (6H, s, $2\times CH_3$), 2.17 (3H, s, OAc), 7.27 (5H, s, Ph), 7.44—8.65 (9H, m, ArH), and 17.05 (1H, s, OH). Found: C, 79.05; H, 5.85%. Calcd for $C_{28}H_{24}O_4$: C, 79.22; H, 5.70%.

9-Acetoxy-9-(2-acetyl-3-oxo-1-phenyl-1-butenyl)-9,10-dihydroanthracene (11; R=Ac): 29%; colorless needles (from benzene/hexane); mp 152—153 °C; IR ($CHCl_3$) 1747 (OAc) and 1680 ($COCH_3$); ^1H-NMR ($CDCl_3$) δ=2.13 (9H, s, OAc and $2\times COCH_3$), 3.24 (2H, s, CH_2), 6.8—7.5 (13H, m, ArH); ^{13}C-NMR ($CDCl_3$) δ=200.875 (s, $\underline{C}OCH_3$), 167.996 (s, $O\underline{C}OCH_3$), 144.338 (s, C=C), 138.937 (s, ArC), 136.560 (s, ArC), 134.621 (s, ArC), 131.187 (d, ArC), 130.102 (s, C=C), 128.721 (d, ArC), 127.636 (d, ArC), 127.167 (d, ArC), 126.814 (d, ArC), 126.697 (d, ArC), 124.316 (d, ArC), 81.372 (s, $-\overset{|}{\underset{|}{C}}-$), 49.520 (t, CH_2), 31.292 (q, $CO\underline{C}H_3$), and 21.722 (q, $OCO\underline{C}H_3$); MS m/z (rel intensity), 424 (M$^+$, 7), 366 (5), 333 (8), 291 (100), 273 (27), and 249 (25). Found: C, 79.05; H, 5.87%; m/z 424.16835. Calcd for $C_{28}H_{24}O_4$: C, 79.22; H, 5.70%; M, 424.16746.

9-(2-Acetyl-3-oxo-1-phenyl-1-butenyl)-9,10-dihydro-9-anthrol 11; R=H): 14%; liquid; IR ($CHCl_3$) 3600—3100 (OH) and 1680 (C=O); ^1H-NMR ($CDCl_3$) δ=2.21 (6H, s, $2\times COCH_3$), 2.53 (1H, br. s, OH), 3.08 (2H, s, CH_2), 6.75—7.55 (13H, m, ArH).

Reaction of Olefins with Acetylacetone in the Presence of Manganese(III) Acetate (Heiba's Method).[5] To a heated solution of olefin (1 mmol) and acetylacetone (4 mmol) in acetic acid (25 cm^3), Mn(OAc)$_3$ (4 mmol) was added. The solution was heated under reflux until the brown color of the Mn(III) ion disappeared. The reaction mixture was then treated by the procedure described above. The products were separated on TLC, and the structure of the compound was determined by means of the ^{1}H-NMR and IR spectra. **2a** (88%) and **3a** (2%) from **1a** (10% recovered); **2b** (89%) from **1b**; **2c** (69%) from **1c**; **2d** (36%) from **1d**; **2e** (55%) from **1e**; **2f** (39%) and **6f** (2%) from **1f** (50% recovered); **2g** (22%), **4g** (38%), and **5g** (10%) from **1g**; **4h** (28%), **5h** (15%), **6h** (2%), and 2,3,3-tris(4-methoxyphenyl)-2-propenal (6%)[2] from **1h**; **2i** (25%) and **6i** (18%) from **1i**; **7j** (67%) from **1j**.

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