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Formation of 1,2-Dioxanes by the Use of Tris(2,4-pentanedionato)manganese(III) or Manganese(III) Acetate

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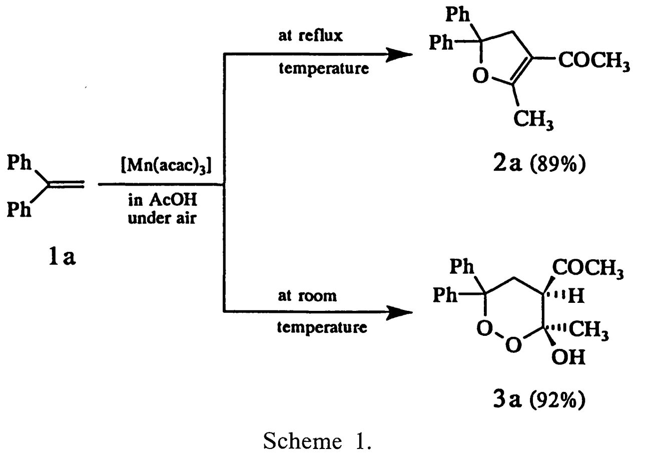
The reactions of 1,1-diphenylethene, 1,1-bis(4-chlorophenyl)ethene, 1,1-bis(4-methoxyphenyl)ethene, 1,1-bis(4-methylphenyl)ethene, 1,1-bis(4-fluorophenyl)ethene, styrene, 1-octene, cyclohexene, and cyclooctene with tris(2,4-pentanedionato)manganese(III) ([Mn(acac)$_3$]) in acetic acid at room temperature give 4-acetyl-3-methyl-1,2-dioxan-3-ol in 8—92% yields, together with 3-acetyl-4-hydroxy-3-hexene-2,5-dione. The similar reactions of 1,1-diphenylethene with 2,4-pentanedione, 3-methyl-2,4-pentanedione, 3-ethyl-2,4-pentanedione, 1-phenyl-1,3-butanedione, acetoacetanilide, and 1,3-cyclohexanedione in the presence of manganese(III) acetate also give the corresponding cyclic peroxide in good to moderate yields. The mechanisms of manganese(III)-induced 1,2-dioxane ring formation and concomitant radical side reaction are discussed.

A unique synthetic methodology utilizing manganese(III)-mediated radical inter- or intra-molecular cyclization reactions has been recently and extensively investigated and modified.1—3) Particularly, manganese(III) acetate and tris(2,4-pentanedionato)manganese(III) ([Mn(acac)$_3$]) are well-known reagents, which perform a very interesting role in acetic acid. That is, two types of reaction occur simultaneously: (1) a one-electron-transfer from an electron-rich organic substrate (donor) to a manganese(III) complex (acceptor) and (2) a radical reaction for ligands which are formed from the thermolysis of a manganese(III) complex or ligand-exchange reaction.4) These reactions are also influenced by reaction temperature or additives such as acetate ions and water. In the course of a study on the reactions of [Mn(acac)$_3$] with various organic substrates, one of the present authors found that the reaction product from alkenes using this reagent at room temperature differed dramatically from that at the elevated temperature.5) When 1,1-diphenylethene (**1a**) was treated with [Mn(acac)$_3$] in acetic acid under air *at the reflux temperature*, it gave 3-acetyl-2-methyl-5,5-diphenyl-4,5-dihydrofuran (**2a**), together with a small amount of benzophenone (**4a**). When the reaction was carried out under air *at room temperature* for 12 h, it gave 4-acetyl-3-methyl-6,6-diphenyl-1,2-dioxan-3-ol (**3a**) (the structure was erroneously assigned as 3-acetyl-2-hydroperoxy-2-methyl-5,5-diphenyltetrahydrofuran in the previous paper5)) along with small amounts of **4a**, 4,4-diphenyl-4-butanolide (**5a**), and 3-acetyl-4-hydroxy-3-hexene-2,5-dione (**8**). Although a lot of cyclic peroxides were synthesized using photosensitized oxygenation6) and electrochemical cycloaddition,7) the present reaction is the first example that molecular oxygen is trapped during the manganese(III)-induced radical intermolecular cyclization.8) We also found that the reaction of **1a** with a 1,3-dicarbonyl compound in the presence of manganese(III) acetate in acetic acid at room temperature gave a similar cyclic peroxide.8) Therefore, we have been intrigued by these reaction mechanisms and in the possibility of their application to organic synthesis. Herein we report the results of our study.



Scheme 1.

Results

Reaction of Alkenes with [Mn(acac)$_3$]. We scrutinized the reaction products from **1a** and found that 4,4-diphenyl-4-butanolide (**5a**), 2,2-diphenyl-2-hydroxyethyl acetate (**6a**), 1-phenyl-1,4-pentanedione (**7a**), and 3-acetyl-4-hydroxy-3-hexene-2,5-dione (**8**) were obtained together with **2a** and **3a** after separation by TLC (Table 1). The structures of these products were determined by analyzing their ^{1}H NMR, IR, and mass spectra as well as by comparing their spectra and melting points with the authentic specimen. The reaction of **3a** with triphenylphosphine gave **2a** (32%), 3-acetyl-2-methyl-5,5-diphenyltetrahydrofuran-2-ol (**9**) (49%), 4-oxo-1,1-diphenylpentyl acetate (**10**) (13%), and triphenylphosphine oxide (83%).6b,c,9) The structure of **3a** was finally confirmed by an X-ray crystallography. A single crystal of **3a** was successfully grown from ethanol in the orthorhombic space group $P2_12_12_1$ with cell constants a=7.856, b=12.823, and c=15.820 Å. The X-ray structure was solved using the SHELXTL direct

Table 1. Reaction of 1,1-Diphenylethene (**1a**) with Tris(2,4-pentanedionato)manganese(III) in AcOH at 23 °C

Entry	Molar ratio[a]	Time	Recovery	Product (yield/%)[b]						
		h	%	**2a**	**3a**	**4a**	**5a**	**6a**	**7a**	**8**[c]
1	1:0.5	4	25		43	9	7	11		5
2	1:1	11			92	3	2			7
3[d]	1:1	5	57		21	4	2	7		26
4	1:2	19		8	83	5		3		13
5	1:3	24		9	78	5			10	17

a) **1a**: $[\mathrm{Mn(acac)_3}]$. b) Isolated yield based on the amount of **1a** used. c) Isolated yield based on the amount of $[\mathrm{Mn(acac)_3}]$ used. d) Reaction under an oxygen atmosphere.

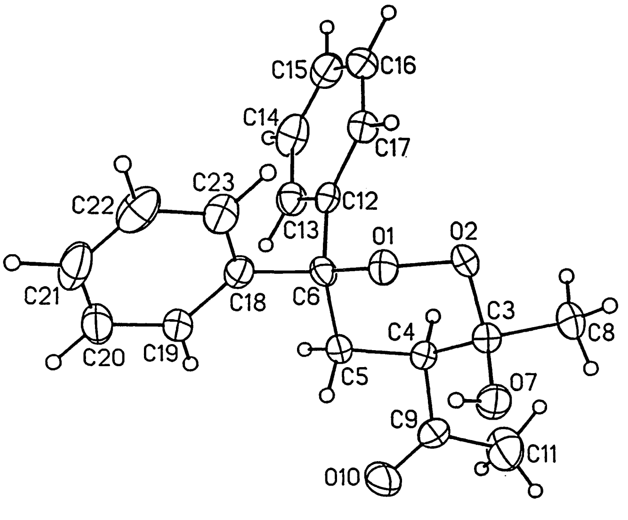
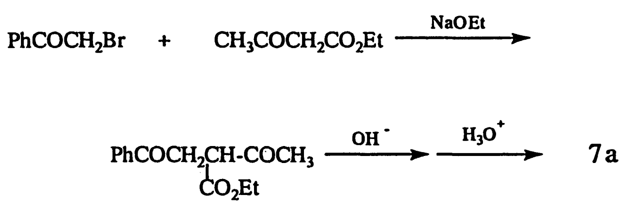


Fig. 1. ORTEP diagram of **3a**. The thermal ellipsoids are 40% equiprobability envelopes, with hydrogens as spheres of arbitrary diameter.

methods program, TREF, which revealed the positions of all of the nonhydrogen atoms. The ORTEP diagram of **3a** is presented in Fig. 1. The O(1)–O(2) bond length is 1.470 Å, the bond angles at O(1) and O(2) are 108.1° and 109.6°, respectively, and the peroxide torsional angle (C(6)-O(1)-O(2)-C(3)) is −74.0°.[10] Unfortunately, we could not determine the absolute configuration because of the lack of a significant anomalous scatterer in the crystal, although **3a** crystallized in a chiral space group (see Experimental Section). However, it should be noted that the cyclic peroxide (**3a**) in the solid state was obtained as the *c*-4-acetyl-3-methyl-1,2-dioxan-*r*-3-ol based on the X-ray analysis. The structure of **7a** was also confirmed by synthesis: the condensation of 2-bromoacetophenone with ethyl 3-oxobutanoate, followed by hydrolysis and acidification, gave **7a** (Scheme 2).



$$\mathrm{PhCOCH_2Br} + \mathrm{CH_3COCH_2CO_2Et} \xrightarrow{\mathrm{NaOEt}} \underset{\mathrm{CO_2Et}}{\mathrm{PhCOCH_2CH\text{-}COCH_3}} \xrightarrow{\mathrm{OH^-}} \xrightarrow{\mathrm{H_3O^+}} \mathbf{7a}$$

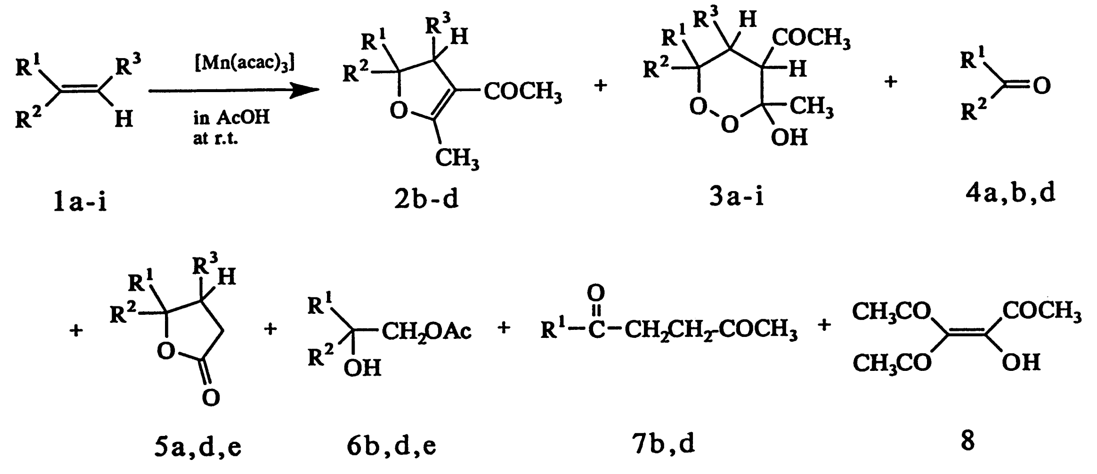
Scheme 2.

The reaction of **1a** with $[\mathrm{Mn(acac)_3}]$ in AcOH at 23 °C under air was then carried out at various molar ratios. The best yield of **3a** was attained when the molar ratio was 1 : 1 (Table 1, Entry 2). The reaction under an oxygen atmosphere gave a decreased yield of **3a** with an increase in the yield of **8** (Entry 3). The yield of **3a** decreased at higher molar ratios (Entries 4 and 5).

The reactions were examined for 1,1-bis(4-chlorophenyl)ethene (**1b**), 1,1-bis(4-methoxyphenyl)ethene (**1c**), 1,1-bis(4-methylphenyl)ethene (**1d**), 1,1-bis(4-fluorophenyl)ethene (**1e**), styrene (**1f**), 1-octene (**1g**), cyclohexene (**1h**), and cyclooctene (**1i**) in AcOH to yield the corresponding 1,2-dioxane derivatives (**3b**—**i**) (Scheme 3). It was observed that the molar ratio at which the maximum yield was attained depended on the substrate as shown in Table 2. The alkenes having no aromatic substituents are poor substrates for the 1,2-dioxane formation (Entries 12—14).

Similar reactions of **1a** with (2,4-pentanedionato)-metals such as $[\mathrm{Cr(acac)_3}]$, $[\mathrm{Co(acac)_3}]$, $[\mathrm{Fe(acac)_3}]$, and $[\mathrm{Cu(acac)_2}]$ were also carried out, but either **1a** was recovered unchanged or a complex mixture resulted.

Reaction of 1a with 1,3-Diketones in the Presence of Manganese(III) Acetate. When the reaction of **1a** with 2,4-pentanedione in the presence of manganese(III) acetate was carried out at a molar ratio of 1 : 3 : 1, the major product was again **3a**, along with small amounts of **5a**, **7a**, and **8** (Table 3). When 3-methyl-2,4-pentanedione in place of 2,4-pentanedione was added during the oxidation of **1a** with manganese(III) acetate, the products were 4-acetyl-3,4-dimethyl-6,6-diphenyl-1,2-dioxan-3-ol (**11a**), 3-acetyl-2-ethoxy-2,3-dimethyl-5,5-diphenyltetrahydrofuran (**12a**), and **4a**. The reaction of 3-ethyl-2,4-pentanedione also yielded the corresponding 1,2-dioxan-3-ol derivative (**11b**) and 2-ethoxytetrahydrofuran (**12b**). The similar reactions of **1a** using 1-phenyl-1,3-butanedione, acetoacetanilide, and 1,3-cyclohexanedione gave the corresponding cyclic peroxides (**11c**—**e**) (Fig. 2).



a : R^1=R^2=Ph, R^3=H
b : R^1=R^2=4-ClC_6H_4, R^3=H
c : R^1=R^2=4-$MeOC_6H_4$, R^3=H
d : R^1=R^2=4-MeC_6H_4, R^3=H,
e : R^1=R^2=4-FC_6H_4, R^3=H

f : R^1=Ph, R^2=R^3=H
g : R^1=C_6H_{13}, R^2=R^3=H
h : R^1,R^3=-$(CH_2)_4$-, R^2=H
i : R^1,R^3=-$(CH_2)_6$-, R^2=H

Scheme 3.

Table 2. Reaction of Alkenes (**1a**—**i**) with Tris(2,4-pentanedionato)manganese(III) in AcOH at 23 °C

Entry	Alkene	Molar ratio[a]	Time/h	Product (yield/%)[b,c]						
6	**1a**	1:1	11		**3a** (92)	**4a** (3)	**5a** (2)			**8** (7)
7	**1b**	1:2	12	**2b** (2)	**3b** (88)	**4b** (3)		**6b** (1)	**7b** (3)	**8** (13)
8	**1c**	1:2	12	**2c** (10)	**3c** (87)					**8** (<1)
9	**1d**	1:1	13	**2d** (3)	**3d** (77)	**4d** (1)	**5d** (1)	**6d** (4)	**7d** (10)	**8** (11)
10	**1e**	1:1	12		**3e** (72)	**4e** (2)	**5e** (2)	**6e** (4)		**8** (14)
11	**1f**	1:1	12		**3f** (34)					**8** (10)
12	**1g**	5:1	15		**3g** (8)					**8** (<1)
13	**1h**	4:1	12		**3h** (11)					**8** (5)
14	**1i**	5:1	14		**3i** (43)					

a) Alkene: [Mn(acac)3]. b) Isolated yield based on the amount of the alkene used except for **8**.
c) The yield of **8** was based on the amount of the [Mn(acac)3] used.

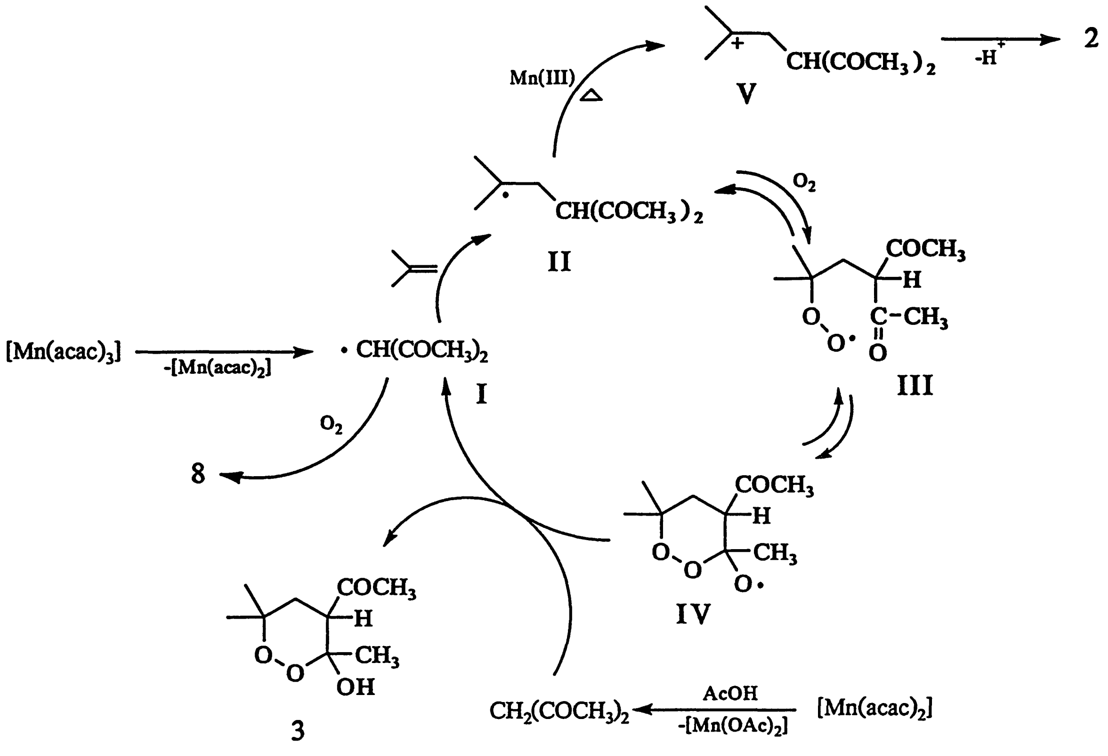
Table 3. Reaction of 1,1-Diphenylethene (**1a**) with 1,3-Dicarbonyl Compounds in the Presence of Manganese(III) Acetate in AcOH at 23 °C

Entry	1,3-Dicarbonyl compound	Molar ratio[a]	Time/h	Product (yield/%)[b]						
15	2,4-Pentanedione	1:3:1	9	**3a** (81)		**4a** (<1)	**5a** (1)	**6a** (1)	**7a** (1)	**8** (3)[c]
16	3-Methyl-2,4-pentanedione	1:4:1	3	**11a** (49)	**12a** (22)	**4a** (5)				
17	3-Ethyl-2,4-pentanedione	1:4:1	3	**11b** (62)	**12b** (26)					
18	1-Phenyl-1,3-butanedione	1:3:1	24	**11c** (43)						
19	Acetoacetanilide	1:3:1	2	**11d** (91)						
20	1,3-Cyclohexanedione	1:3:1	12	**11e** (49)		**4a** (12)				

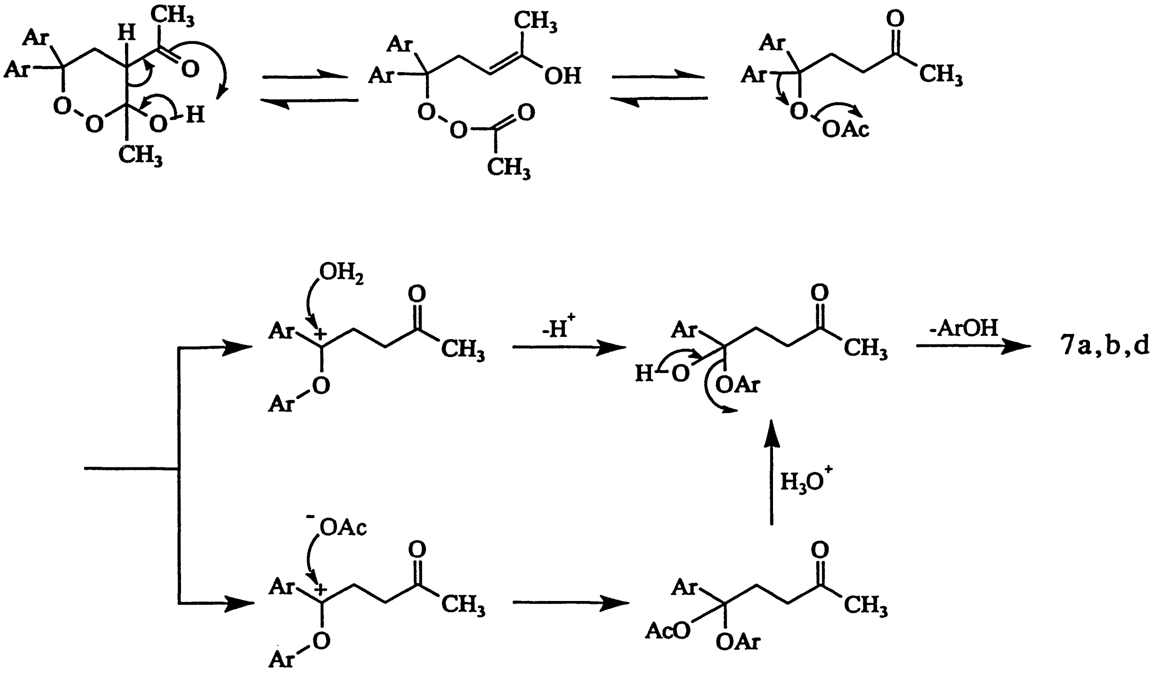
a) **1a**: 1,3-Dicarbonyl compound: Manganese(III) acetate. b) Isolated yield based on the amount of **1a** used.
c) Isolated yield based on the amount of 2,4-pentanedione used.

Discussion

The mechanism for the formation of 1,2-dioxanes in the [Mn(acac)3] system can be depicted as the following. The decomposition of [Mn(acac)3] would produce diacetylmethyl radicals (**I**) which attack the double bond in alkenes, resulting in tertiary radicals (**II**).[4d,5] The radicals (**II**) then react with oxygen to give radicals (**III**),[7a,b] which are cyclized to alkoxyl radicals (**IV**) and could give 1,2-dioxanes (**3**) after abstraction of hydrogen from the solvent and/or 2,4-pentanedione which results from the ligand-exchange reaction of [Mn(acac)$_2$]. The radicals (**II**), on the other hand, can be oxidized to carbocations (**V**) with Mn(III) at elevated temperatures since concentration of dissolved oxygen in AcOH is probably small at high temperatures, which eventually give rise to dihydrofuran derivatives (**2**) (Scheme 4). When the reaction of **1b** with [Mn(acac)$_3$] (1 : 2 molar ratio) was carried out at 23 °C for 12 h under an argon atmosphere, **1b** (38%) was recovered and **2b** (57%) was obtained (see Experimental Section). Any existence of **3b** was not detected. This indicates that the oxygens in the 1,2-dioxane ring did come from molecular oxygen in the air. Unexpectedly, the reac-



Scheme 4.

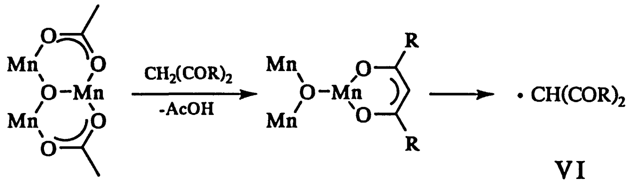


Scheme 5.

tion under an atmosphere of pure oxygen decreased the yield of **3a** and increased the yield of **8**. This may suggest that diacetylmethyl radicals (**I**) formed by the decomposition of [Mn(acac)$_3$] are consumed during dimerization followed by the oxidation with oxygen and the rearrangement, eventually giving **8**. It is worth noting that **3a** was obtained as the *c*-4-acetyl-3-methyl-1,2-dioxan-*r*-3-ol based on the X-ray analysis. This means that the cyclization of peroxyl radical (**III**) is reversible and leads to a thermodynamically stable configuration, that is to say, the *c*-4-acetyl-1,2-dioxan-*r*-3-ol form.[7b]

The formations of 2,2-diaryl-2-hydroxyethyl acetates (**6b**, **d**, **e**) and benzophenones (**4a**, **b**, **d**, **e**) have been well accounted for by the electron-transfer mechanism in the oxidation of **1a** and subsequent cleavage of the resulting diol monoacetate by Mn(III).[11] 4,4-Diaryl-4-butanolides (**5a**, **d**, **e**) are the products of the reaction of alkenes with carboxymethyl radicals, ·CH$_2$COOH.[4a—c,12] The formation of 1-aryl-1,4-pentanediones (**7a**, **b**, **d**) showed another feature of the reaction. Probably, they might be formed by retro-Claisen type reaction, followed by Criegee type peroxy ester rearrangement of the corresponding 1,2-dioxanes,[6e] although its mechanism is not yet clarified at present (Scheme 5).

In the case of the manganese(III) acetate system, the ligand-exchange reaction of acetate ligands on manganese(III) acetate and 1,3-dicarbonyl compounds must occur first, because manganese(III) acetate, which is insoluble in AcOH at ambient temperature, does dissolve in the solution of 1,3-diketone–AcOH at room temperature. Although no isolated manganese(III) acetate–1,3-diketone complexes have been reported, it is known that bis(2,4-pentanedionato)manganese(III) carboxylate complexes can be prepared by the ligand-exchange reaction from [Mn(acac)$_3$] and the corresponding carboxylic acids.[13] Slow decomposition of the diketone–Mn(III) complex then yields the corresponding 1,3-diketo radicals(**VI**). This is consistent with previously proposed mechanism by us[2f,4d,h,14] and others.[2c,4g,15] The radicals **VI** attack the alkene in a similar manner as shown in Scheme 4 to give the cyclic peroxides (**3a**, and **11a**—**e**). The ethoxyl groups in **12a** and **12b** probably come from ethanol which was used as the recrystallizing solvent.



VI

Scheme 6.

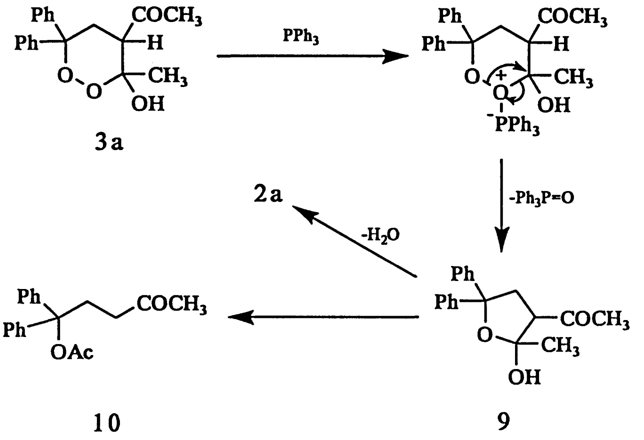
Electrochemical oxidation of 2-alkyl-1,3-diketones in the presence of alkenes under an oxygen atmosphere has been reported and this also gave the substituted 1,2-dioxane ring system.[7] The structure of the cyclic peroxide derivative was determined by X-ray analysis. The reaction is also affected by adding azobis(isobutyronitrile) (AIBN) as a radical initiator.[7b] However, the reactions seem to be limited to the 1,3-diketones which produce tertiary radicals during electrochemical oxidation.

11a: R^1=R^2=R^3=CH$_3$
11b: R^1=Et, R^2=R^3=CH$_3$
11c: R^1=H, R^2=CH$_3$, R^3=Ph
11d: R^1=H, R^2=CH$_3$, R^3=NHPh
11e: R^1=H, R^2,R^3=-CH$_2$CH$_2$CH$_2$-

12a: R=CH$_3$
12b: R=Et

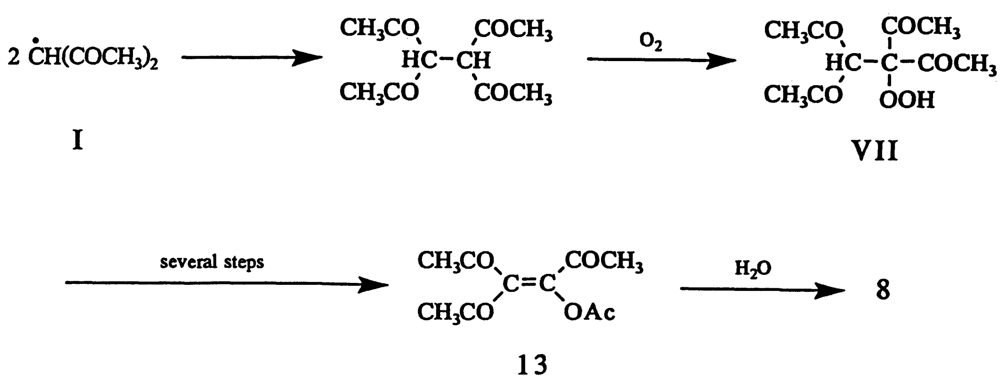
Fig. 2.

The reduction of **3a** with triphenylphosphine deserves comments. The cyclic peroxide (**3a**) can be coordinated to triphenylphosphine with using one of the oxygens in the 1,2-dioxane ring and subsequent rearrangement would give **9** and then **2a**. The formation of **10** would be explained as the result of retro-Claisen reaction of **9** such as the formation of **7** from **3**. These reactions are shown in Scheme 7.



Scheme 7.

We also looked into the mechanisms in which **8** was formed. The hexanedione **8** was formed irrespective of the substrate used. When oxygen was passed through the reaction mixture, the reaction time was decreased by half and the maximum yield of **8** was attained. During the anhydrous work-up of the reaction of [Mn(acac)$_3$] it afforded 3-acetoxy-4-acetyl-3-hexene-2,5-dione (**13**). Therefore, the mechanism can be visualized as shown in Scheme 8. The diacetylmethyl radicals (**I**) dimerize and are then oxidized to a hydroperoxide (**VII**). The hydroperoxide (**VII**) rearranges to **13** and is finally hydrolyzed to give **8** that was formed during the work-up. The acyl migration of this type is probably the first example that occurs in a polyketonic



Scheme 8.

compound.

This 1,2-dioxane framework reminds us of bioactive natural occurring cyclic peroxides such as root-growth inhibitor.[16a,b] Therefore, we examined the biological activities for insecticide, bactericide, and herbicide of the 1,2-dioxanes (**3a**—**e**). Contrary to our expectation, no activity was observed for these compounds.[17] However, we believe that this synthetic method can be used as one of the preparative techniques for natural occurring cyclic peroxides.

Conclusions

The reactions of 1,1-diarylethenes, arylethenes, and alkenes, though to limited extent, with tris(2,4-pentanedionato)manganese(III) or with 1,3-diketones in the presence of manganese(III) acetate at room temperature gave 1,2-dioxane derivatives in moderate to good yields. They may provide a useful tool for the synthesis of a new type peroxide, i.e. 1,2-dioxane derivatives.

Experimental

Instrumentation. Infrared spectra were recorded in chloroform except for **12a** on either a JASCO A-102 or a JASCO FT/IR-7000 infrared spectrometer. The IR spectral data are expressed in cm^{-1}. ^{1}H NMR spectra were measured in chloroform-*d*, DMSO-d_6, or carbon tetrachloride on either a JEOL JNM-PMX60SI or a Nicolet 300MHz NMR spectrometer at room temperature. Chemical shifts are reported in ppm downfield from an internal TMS standard. Mass spectra were measured on either a JEOL JMS-DX303HF or a Finnigan 6000 GC/MS mass spectrometer at an ionizing voltage of 70 eV. All melting points were determined with a Yanaco MP-J3 micromelting point apparatus (Yanagimoto) and were uncorrected. Elemental analyses were performed by Elemental Analysis Center, Faculty of Science, Kyushu University.

Materials. Tris(2,4-pentanedionato)manganese(III)[18] and manganese(III) acetate[4a] were prepared according to the method previously described. 1,1-Diarylethenes (**1a**—**e**) were prepared by dehydration of the corresponding alcohols which were synthesized from substituted acetophenones and arylmagnesium bromides.[5] Styrene (Wako), 1-octene (Wako), cyclohexene (Wako), cyclooctene (Wako), and acetic acid (Kanto) were used as received.

Oxidation of Alkenes with Tris(2,4-pentanedionato)manganese(III) ([Mn(acac)$_3$]). A typical procedure for the oxidation of alkenes with [Mn(acac)$_3$] was as follows. An alkene (1 mmol) was dissolved in acetic acid (25 mL) in a 100 mL round-bottomed flask equipped with a calcium chloride drying tube followed by addition of [Mn(acac)$_3$] (1 mmol) to the mixture. The mixture was stirred at 23 °C under air until the brown color of the Mn(III) species turned a transparent pale yellow. The reaction time is shown in Tables 1 and 2. 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 (Wakogel B-10) with chloroform as the developing solvent.

Oxidation Products. 3-Acetyl-2-methyl-5,5-diphenyl-4,5-dihydrofuran (2a): Yellow liquid; (lit,[5] bp 180—185 °C/133 Pa).

4-Acetyl-3-methyl-6,6-diphenyl-1,2-dioxan-3-ol (3a): Colorless prisms (EtOH); mp 165—166 °C (lit,[5] mp 161—162 °C).

Benzophenone (4a): Colorless needles (EtOH); mp 48 °C.[19]

4,4-Diphenyl-4-butanolide (5a): Colorless prisms (EtOH); mp 90—91 °C (lit,[20] mp 87—90 °C).

2,2-Diphenyl-2-hydroxyethyl Acetate (6a): Colorless prisms (EtOH); mp 92.0—92.5 °C (lit,[21] mp 93—93.5 °C).

1-Phenyl-1,4-pentanedione (7a): Pale yellow liquid; bp 116 °C/66.7 Pa (lit,[22] bp 93—94 °C/13.3 Pa).

3-Acetyl-4-hydroxy-3-hexene-2,5-dione (8): Colorless prisms (benzene); mp 116.0—116.3 °C (lit,[4d] mp 115—116 °C).

3-Acetyl-5,5-bis(4-chlorophenyl)-2-methyl-4,5-dihydrofuran (2b): Colorless cubes; mp 95—96 °C (petroleum ether). IR (CHCl$_3$) ν=1670 (COMe). ^{1}H NMR (CDCl$_3$) δ=2.20 (3H, s, COMe), 2.33 (3H, t, J=1.6 Hz, Me), 3.56 (2H, q, J=1.6 Hz, -CH$_2$-), 7.28 (8H, s, arom.H). MS m/z (rel intensity) 346 (M$^+$) (91), 303 (67), 275 (26), 225 (26). Found: m/z 346.0526. Calcd for $C_{19}H_{16}O_2{}^{35}Cl_2$: M, 346.0527.

4-Acetyl-6,6-bis(4-chlorophenyl)-3-methyl-1,2-dioxan-3-ol (3b): Colorless needles (EtOH); mp 164—165 °C. IR (CHCl$_3$) ν=3592—3600 (OH), 1699 (COMe). ^{1}H NMR (CDCl$_3$) δ=1.28 (3H, s, Me), 2.29 (3H, s, COMe), 2.27 (3H, m, -CH$_2$-CH<), 4.12 (1H, br, OH), 7.00—7.50 (8H, m, arom.H). MS m/z (rel intensity) 380 (M$^+$) (1), 347 (23), 305 (60), 250 (47), 139 (100). Found: C, 59.81; H, 4.79%. Calcd for $C_{19}H_{18}O_4Cl_2$: C, 59.86; H, 4.76%.

4,4′-Dichlorobenzophenone (4b): Colorless needles (benzene–hexane); mp 144.3—145.3 °C (lit,[23] mp 146.5 °C).

2,2-Bis(4-chlorophenyl)-2-hydroxyethyl Acetate (6b):

Colorless prisms (EtOH); mp 95.5—96.2 °C. IR ($CHCl_3$) ν=3604—3200 (OH), 1743 (OAc). ^{1}H NMR ($CDCl_3$) δ=2.00 (3H, s, OAc), 3.30 (1H, br, OH), 4.62 (2H, s, -CH_2-), 7.32 (8H, s, arom.H). Found: C, 59.11; H, 4.30%. Calcd for $C_{16}H_{14}O_3Cl_2$: C, 59.08; H, 4.33%.

1-(4-Chlorophenyl)-1,4-penanedione (7b): Colorless needles (EtOH); mp 74.5—75.0 °C (lit,[22] mp 76 °C).

3-Acetyl-5,5-bis(4-methoxyphenyl)-2-methyl-4,5-dihydrofuran (2c): Colorless needles (benzene–petroleum ether); mp 96—97 °C (lit,[5] mp 96.0—96.5 °C).

4-Acetyl-6,6-bis(4-methoxyphenyl)-3-methyl-1,2-dioxan-3-ol (3c): Pale yellow liquid. IR ($CHCl_3$) ν=3584—3200 (OH), 1700 (COMe). ^{1}H NMR ($CDCl_3$) δ=1.27 (3H, s, Me), 2.25 (3H, s, COMe), 2.75 (3H, m, -CH_2-CH⟨), 3.75 (6H, s, 2×OMe), 4.43 (1H, br, OH), 6.50—7.50 (8H, m, arom.H). MS *m*/*z* (rel intensity) 372 (M^+) (1), 312 (9), 242 (52), 211 (21), 188 (33). Found: *m*/*z* 372.1570. Calcd for $C_{21}H_{24}O_6$: M, 372.1571.

3-Acetyl-2-methyl-5,5-bis(4-methylphenyl)-4,5-dihydrofuran (2d): Pale yellow liquid. IR ($CHCl_3$) ν=1664 (COMe). ^{1}H NMR (CCl_4) δ=2.11 (3H, s, COMe), 2.22 (6H, s, 2×Me), 2.27 (3H, t, *J*=1.6 Hz, Me), 3.35 (2H, q, *J*=1.6 Hz, -CH_2-), 6.90—7.33 (8H, m, arom.H). MS *m*/*z* (rel intensity) 306 (M^+) (1), 211 (10), 175 (9), 119 (100). Found: *m*/*z* 306.1604. Calcd for $C_{21}H_{22}O_2$: M, 306.1620.

4-Acetyl-3-methyl-6,6-bis(4-methylphenyl)-1,2-dioxan-3-ol (3d): Colorless needles (EtOH); mp 138—139 °C. IR ($CHCl_3$) ν=3580—3200 (OH), 1669 (COMe). ^{1}H NMR ($CDCl_3$) δ=1.27 (3H, s, Me), 2.25 (6H, s, 2×Me), 2.34 (3H, s, COMe), 2.76 (3H, s, -CH_2-CH⟨), 4.40 (1H, br, OH), 7.06—7.50 (8H, m, arom.H). MS *m*/*z* (rel intensity), 340 (M^+) (1), 307 (23), 265 (7), 210 (47), 119 (100). Found: C, 73.87; H, 7.14%. Calcd for $C_{21}H_{24}O_4$: C, 74.09; H, 7.11%.

4,4′-Dimethylbenzophenone (4d): Colorless needles; mp 92—94 °C.[24]

4,4-Bis(4-methylphenyl)-4-butanolide (5d): Colorless liquid; (lit,[25] bp 183 °C/67 Pa).

2,2-Bis(4-methylphenyl)-2-hydroxyethyl Acetate (6d): Colorless prisms (benzene–hexane); mp 71.0 °C. IR ($CHCl_3$) ν=3610 (OH), 1742 (OAc). ^{1}H NMR ($CDCl_3$) δ=1.97 (3H, s, OAc), 2.28 (6H, s, 2×Me), 3.57 (1H, br, OH), 4.60 (2H, s, -CH_2-), 7.00—7.33 (8H, m, arom.H). MS *m*/*z* (rel intensity) 284 (M^+) (1), 224 (2), 211 (100), 119 (50), 91 (18). Found: C, 76.09; H, 7.08%. Calcd for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09%.

1-(4-Methylphenyl)-1,4-pentanedione (7d): Colorless liquid; (lit,[26] mp 53 °C).

4-Acetyl-6,6-bis(4-fluorophenyl)-3-methyl-1,2-dioxan-3-ol (3e): Colorless prisms (EtOH); mp 142—144 °C. IR ($CHCl_3$) ν=3550—3200 (OH), 1702 (COMe). ^{1}H NMR ($CDCl_3$) δ=1.30 (3H, s, Me), 2.28 (3H, s, COMe), 2.75 (3H, m, -CH_2-CH⟨), 4.23 (1H, br, OH), 7.10—8.00 (8H, m, arom.H). Found: C, 65.53; H, 5.23%. Calcd for $C_{19}H_{18}O_4F_2$: C, 65.51; H, 5.21%.

4,4′-Difluorobenzophenone (4e): Colorless needles; mp 103—105 °C.[27]

4,4-Bis(4-fluorophenyl)-4-butanolide (5e): Yellow liquid. IR ($CHCl_3$) ν=1778 (-O-CO-). ^{1}H NMR (CCl_4) δ=2.25—3.02 (4H, m, -CH_2-CH_2-), 6.83—7.87 (8H, m, arom.H). MS *m*/*z* (rel intensity) 274 (M^+) (45), 219 (100), 123 (58). Found: *m*/*z* 274.0813. Calcd for $C_{16}H_{12}O_2F_2$: M, 274.0805.

2,2-Bis(4-fluorophenyl)-2-hydroxyethyl Acetate (6e): Colorless needles (petroleum ether); mp 71—72 °C. IR ($CHCl_3$) ν=3596—3200 (OH), 1741 (OAc). ^{1}H NMR ($CDCl_3$) δ=2.01 (3H, s, OAc), 4.00 (1H, br, OH), 4.63 (2H, s, -CH_2-), 7.10—7.60 (8H, m, arom.H). Found: C, 65.86; H, 4.92%. Calcd for $C_{16}H_{14}O_3F_2$: C, 65.75; H, 4.83%.

4-Acetyl-3-methyl-6-phenyl-1,2-dioxan-3-ol (3f): Colorless prisms (EtOH); mp 110—111 °C. IR ($CHCl_3$) ν=3592—3200 (OH), 1698 (COMe). ^{1}H NMR ($CDCl_3$) δ=1.45 (3H, s, Me), 2.28 (3H, s, COMe), 1.77—3.27 (3H, m, -CH_2-CH⟨), 4.10 (1H, s, OH), 5.06 (1H, m, H-5), 7.32 (5H, m, Ph). MS *m*/*z* (rel intensity) 237 (M+1) (6), 219 (49), 203 (74), 161 (47). Found: C, 66.00; H, 6.76%. Calcd for $C_{13}H_{16}O_4$: C, 66.08; H, 6.83%.

4-Acetyl-6-hexyl-3-methyl-1,2-dioxan-3-ol (3g). Pale yellow liquid. IR ($CHCl_3$) ν=3580—3200 (OH), 1691 (COMe). ^{1}H NMR (CCl_4) δ=1.06—2.00 (13H, m, C_6H_{13}), 1.39 (3H, s, Me), 2.24 (3H, s, COMe), 2.33—3.20 (3H, m, -CH_2-CH⟨), 4.00 (1H, br, H-5), 4.33 (1H, br, OH). MS *m*/*z* (rel intensity), 244 (M^+) (1), 185 (9), 113 (100), 71 (100), 43 (96). Found: *m*/*z* 244.1671. Calcd for $C_{13}H_{24}O_4$: M, 244.1674.

5-Acetyl-4-methyl-2,3-dioxabicyclo[4.4.0]decan-4-ol (3h): Pale yellow liquid. IR ($CHCl_3$) ν=3576—3150 (OH), 1692 (COMe). ^{1}H NMR (CCl_4) δ=0.66—4.00 (11H, m, C_6H_{10}, H-5), 1.26 (3H, s, Me), 2.19 (3H, s, COMe), 5.57 (1H, br, OH). MS *m*/*z* (rel intensity) 214 (M^+) (1), 197 (7), 155 (22), 111 (33), 97 (100). Found: *m*/*z* 214.1138. Calcd for $C_{11}H_{18}O_4$: M, 214.1204.

12-Acetyl-11-methyl-9,10-dioxabicyclo[6.4.0]dodecan-11-ol (3i): Pale yellow liquid. IR ($CHCl_3$) ν=3600—3200 (OH), 1699 (COMe). ^{1}H NMR ($CDCl_3$) δ=1.07—3.33 (15H, m, C_8H_{14}, H-12), 1.27 (3H, s, Me), 2.22 (3H, s, COMe), 3.83 (1H, br, OH). MS *m*/*z* (rel intensity), 225 (M^+ −17) (20), 183 (8), 167 (13), 121 (17), 97 (50), 71 (55), 43 (100).

Reaction of 1,1-Diphenylethene (1a) with 1,3-Diketones in the Presence of Manganese(III) Acetate.[28] To a mixture of **1a** (1 mmol) and 1,3-diketone (3 or 4 mmol) in acetic acid (25 mL), manganese(III) acetate (1 equivalent) was added. The solution was stirred at 23 °C under air until the brown color of manganese(III) acetate turned colorless. The reaction mixture was then worked-up by the procedure previously described.

Oxidation Products. 4-Acetyl-3,4-dimethyl-6,6-diphenyl-1,2-dioxan-3-ol (11a): Colorless prisms (EtOH); mp 147.8 °C. IR ($CHCl_3$) ν=3596—3200 (OH), 1696 (COMe). ^{1}H NMR ($CDCl_3$) δ=0.93 (3H, s, Me), 1.40 (3H, s, Me), 2.18 (3H, s, COMe), 2.73 (1H, d, *J*=14.2 Hz, H-4), 3.22 (1H, d, *J*=14.2 Hz, H-4), 4.33 (1H, br, OH), 7.06—7.66 (10H, m, 2×Ph). MS *m*/*z* (rel intensity) 326 (M^+) (1), 293 (74), 251 (18), 105 (100). Found: C, 73.73; H, 6.84%. Calcd for $C_{20}H_{22}O_4$: C, 73.60; H, 6.79%.

3-Acetyl-2-ethoxy-2,3-dimethyl-5,5-diphenyltetrahydrofuran (12a): Colorless prisms (EtOH); mp 123.5—124.5 °C. IR (KBr) ν=1711 (COMe). ^{1}H NMR ($CDCl_3$) δ=0.55 (3H, t, *J*=7.2 Hz, -$OCH_2\underline{CH_3}$), 0.97 (3H, s, Me), 1.62 (3H, s, Me), 2.17 (3H, s, COMe), 2.62 (1H, d, *J*=13.0 Hz, H-4), 3.34 (2H, q, *J*=7.2 Hz, -$O\underline{CH_2}CH_3$), 3.82 (1H, d, *J*=13.0 Hz, H-4), 7.00—7.67 (10H, m, 2×Ph). MS *m*/*z* (rel intensity) 338 (M^+) (1), 293 (100), 250 (32). Found: C, 78.13; H, 7.74%. Calcd for $C_{22}H_{26}O_3$: C, 78.07; H, 7.74%.

4-Acetyl-4-ethyl-3-methyl-6,6-diphenyl-1,2-dioxan-3-ol (11b): Colorless prisms (EtOH); mp 144.2 °C. IR ($CHCl_3$) ν=3632—3200 (OH), 1693 (COMe). ^{1}H NMR ($CDCl_3$) δ=0.33—1.91 (5H, m, Et), 1.51 (3H, s, Me), 1.98 (3H, s, COMe), 2.83 (1H, d, *J*=14.2 Hz, H-4), 3.20 (1H, d, *J*=14.2 Hz, H-4), 5.20 (1H, br, OH), 7.13—7.67 (10H, m, 2×Ph). MS *m*/*z* (rel intensity) 340 (M^+) (2), 265 (15), 180 (78), 105 (100). Found: C, 74.19; H, 7.05%. Calcd for $C_{21}H_{24}O_4$: C, 74.09; H, 7.11%.

3-Acetyl-2-ethoxy-3-ethyl-2-methyl-5,5-diphenyltetrahydrofuran (12b): Colorless liquid. IR ($CHCl_3$) ν=1706 (COMe). ^{1}H NMR (CCl_4) δ=0.28—2.00 (5H, m, Et), 0.37 (3H, t, *J*=7.0 Hz, $-OCH_2\underline{CH_3}$), 1.55 (3H, s, Me), 2.05 (3H, s, COMe), 2.27 (1H, d, *J*=12.0 Hz, H-4), 3.31 (2H, q, *J*=7.0 Hz, $-O\underline{CH_2}CH_3$), 3.58 (1H, d, *J*=12.0 Hz, H-4), 6.97—7.54 (10H, m, 2×Ph). MS *m*/*z* (rel intensity) 352 (M^+) (2), 307 (30), 264 (100). Found: *m*/*z* 352.2055. Calcd for $C_{23}H_{28}O_3$: M, 352.2037.

4-Benzoyl-3-methyl-6,6-diphenyl-1,2-dioxan-3-ol (11c): Colorless needles (EtOH); mp 139—141 °C. IR (KBr) ν=3420 (OH), 1659 (C=O). ^{1}H NMR ($CDCl_3$) δ=1.33 (3H, s, Me), 2.70—4.17 (3H, m, $-CH_2CH\langle$), 7.12 (1H, s, OH), 7.17—8.13 (15H, m, 3×Ph). Found: C, 76.80; H, 5.99%. Calcd for $C_{24}H_{22}O_4$: C, 76.98; H, 5.92%.

4-*N*-Phenylcarbamoyl-3-methyl-6,6-diphenyl-1,2-dioxan-3-ol (11d): Colorless microcrystals (EtOH); mp 191 °C. IR ($CHCl_3$) ν=3600—3100 (NH and OH), 1670 (C=O). ^{1}H NMR ($CDCl_3$) δ=1.33 (3H, s, Me), 2.53—3.50 (3H, m, $-CH_2-CH\langle$), 4.90 (1H, br, OH), 6.93—7.63 (15H, m, 3×Ph), 8.87 (1H, s, NH). Found: C, 73.71; H, 5.97; N, 3.55%. Calcd for $C_{24}H_{23}O_4N$: C, 74.02; H, 5.95; N, 3.60%.

1-Hydroxy-4,4-diphenyl-2,3-dioxabicyclo[4.4.0]decan-7-one (11e): Colorless microcrystals (EtOH); mp 184—186 °C. IR (KBr) ν=3600—3200 (OH), 1705 (C=O). ^{1}H NMR (DMSO-d_6) δ=1.36—2.97 (9H, m, C_5H_9), 6.67 (1H, s, OH), 7.06—7.70 (10H, m, 2×Ph). Found: C, 73.92; H, 6.26%. Calcd for $C_{20}H_{20}O_4$: C, 74.05; H, 6.22%.

In the reaction of **1a** with 3-methyl-2,4-pentanedione or 1,3-cyclohexanedione in the presence of manganese(III) acetate, a small amount of benzophenone (**4a**) was also obtained.

Reaction of 1,1-Bis(4-chlorophenyl)ethene (1b) with [Mn(acac)$_3$] under Argon Atmosphere. [Mn(acac)$_3$] was recrystallized from benzene/petroleum ether[29] and stored under argon. The [Mn(acac)$_3$] (454.2 mg) and **1b** (167.5 mg) were put in a 100 mL Schlenk flask under argon. Acetic acid (25 mL), which was purified by distillation from acetic anhydride–chromium trioxide and stored under argon, was added to the flask by a syringe. The mixture was stirred at 23 °C under argon for 12 h. The solvent was removed under high vacuum and the residue was triturated with 2M HCl (25 mL). The aqueous solution was extracted with chloroform. The crude products were separated on TLC using chloroform as the developing solvent to give **1b** (63.6 mg; 38% recovered) and **2b** (132.9 mg; 57%).

Reduction of 3a with Triphenylphosphine. A mixture of **3a** (0.5 mmol) and Ph_3P (0.5 mmol) in anhydrous diethyl ether (30 mL) was stirred at room temperature overnight. The solvent was removed and the residue was triturated with 2 M hydrochloric acid. The mixture was then extracted with chloroform. The following products were obtained after the separation on a silica-gel column.

3-Acetyl-2-methyl-5,5-diphenyltetrahydrofuran-2-ol (9): Colorless liquid. IR ($CHCl_3$) ν=3610—3200 (OH), 1706 (COMe). ^{1}H NMR (CCl_4) δ=1.73 (3H,s, Me), 2.18 (3H, s, COMe), 2.63—3.18 (3H, m, $-CH_2CH\langle$), 3.27 (1H, br, OH), 7.07—7.73 (10H, m, 2×Ph). MS *m*/*z* (rel intensity) 296 (M^+) (7), 254 (4), 196 (60), 183 (100), 105 (65). Found: *m*/*z* 296.1385. Calcd for $C_{19}H_{20}O_3$: M, 296.1411.

4-Oxo-1,1-diphenylpentyl Acetate (10): Liquid. IR ($CHCl_3$) ν=1737 (O-$\underline{C}$OMe), 1716 (COMe), 1243 ($\underline{O-C}$OMe). ^{1}H NMR ($CDCl_3$) δ=2.01 (3H, s, Me), 2.12 (3H, s, COMe), 2.17—3.33 (4H, m, $-CH_2-CH_2-$), 7.00—7.56 (10H, m, 2×Ph). FAB MS (solvent: $CHCl_3$; matrix: G+T, G+0.5M-NaI), *m*/*z* (rel intensity) 319 (M+Na) (21), 279 (26), 259 (56), 237 (100). Found: *m*/*z* 296.1412. Calcd for $C_{19}H_{20}O_3$: M 296.1394.

Triphenylphosphine Oxide: Colorless prisms (EtOH); mp 152—153 °C (lit,[30] mp 154—155 °C).

Synthesis of 1-Phenyl-1,4-pentanedione (7a). The pentanedione (**7a**) was prepared as follows. To a heated solution of ethyl 3-oxobutanoate (0.06 mol) and metallic sodium (0.05 mol) in anhydrous ethanol, 2-bromoacetophenone (0.05 mol) in anhydrous ethanol was added dropwise. After a few hours reflux, the solvent was removed. The residue was triturated with 2 M sulfuric acid and extracted with benzene. After the removal of the solvent, the reaction mixture was added to a 2 M aqueous sodium hydroxide and stirred at room temperature overnight. The reaction mixture was extracted with benzene, the aqueous solution was acidified with 2 M sulfuric acid and then extracted with diethyl ether. The ethereal solution was dried over anhydrous sodium sulfate. 1-Phenyl-1,4-pentanedione (**7a**, 39%), 3-phenyl-2-cyclopentenone (2%), and 4-oxo-4-phenylbutanoic acid (2%) were obtained after the separation on a silica-gel column.

3-Phenyl-2-cyclopentenone: Colorless prisms (diethyl ether); mp 77.5—78.0 °C (lit,[31] mp 83—84 °C).

4-Oxo-4-phenylbutanoic Acid: Colorless prisms (EtOH); mp 112—113 °C (lit,[32] mp 116.5 °C).

Formation of 13 by Anhydrous Work-up. [Mn(acac)$_3$] (8 mmol) in acetic acid (100 mL) was stirred at 23 °C under air until the brown color of Mn(III) turned yellow. The solvent was removed in vacuo and benzene (150 mL) was added to the residue. After separation of [Mn(OAc)$_2$] by filtration, the solvent was removed under reduced pressure. The residue obtained was purified on TLC to afford a trace amount of **13** and **8**. The product, **13**, was prepared by acetylation of **8** with acetyl chloride: A mixture of **8** and acetyl chloride was heated under reflux for 3 h and then concentrated to dryness. It gave **13**.

3-Acetoxy-4-acetyl-3-hexene-2,5-dione (13): Pale yellow liquid. IR ($CHCl_3$) ν=1687, 1723 (COMe), 1768 (OAc). ^{1}H NMR ($CDCl_3$) δ=1.54 (3H, s, COMe), 2.12 (3H, s, OAc), 2.43 (3H, s, COMe), 2.57 (3H, s, COMe). MS *m*/*z* (rel intensity) 212 (M^+) (2), 170 (12), 127 (63), 43 (100). Found: *m*/*z* 212.0685. Calcd for $C_{10}H_{12}O_5$: M, 212.0688.

X-Ray Crystallography of 3a.[33] A clear colorless thin plate of **3a** having the approximate dimensions 0.56×0.44×0.13 mm was mounted in a random orientation on a Nicolet R3m/v automatic diffractometer. The radiation used was Mo *Kα* monochromatized by a highly ordered graphite crystal. Final cell constants, as well as other information pertinent to data collection and refinement, are listed in Table 4. The Laue symmetry was determined to be *mmm*, and from the systematic absences noted, the space group was shown unambiguously to be $P2_12_12_1$. Intensities were measured using the omega scan technique with the scan rate depending on the count obtained in rapid pre-scans of each reflection. Two standard reflections were monitored after every two hours or after every 100 data points collected. These showed no significant variation. In reducing the data, Lorentz and polarization corrections were applied, however, no correction for absorption was made due to the small absorption coefficient.

Table 4. Data Collection and Processing Parameters

Space group	$P2_12_12_1$, orthorhombic
Cell constants	a=7.856(3) Å b=12.823(6) Å c=15.820(8) Å V=1594 Å^3
Molecular formula	$C_{19}H_{20}O_4$
Formula weight	312.39
Formula units per cell	$Z=4$
Density	ρ=1.30 g cm^{-3}
Absorption coefficient	μ=0.85 cm^{-1}
Radiation (Mo $K\alpha$)	λ=0.71073 Å
Collection range	$4°<2\theta<55°$
Scan width	$\Delta\theta=1.30+(K\alpha_2-K\alpha_1)_o$
Scan speed range	1.5 to 15.0° min^{-1}
Total data collected	2092
Independent data, $I>3\sigma(I)$	1392
Total variables	215
$R=\sum\|\|F_o\|-\|F_c\|\|/\sum\|F_o\|$	0.043
$R_w=[\sum w(\|F_o\|-\|F_c\|)^2/\sum w\|F_o\|^2]^{1/2}$	0.031
Weights	$w=\sigma(F)^{-2}$

The structure was solved by use of the SHELXTL direct methods program TREF, which revealed the positions of all of the nonhydrogen atoms. The usual sequence of isotropic and anisotropic refinement was followed, after which all hydrogens were entered in ideal calculated positions and constrained to riding motion with a single variable isotropic temperature factor. In the final cycles of the least squares the hydroxyl hydrogen H7 was freely refined in order to get accurate hydrogen bonding parameters. The C11 methyl group was treated as a separate rigid body and allowed to rotate freely. Although **3a** crystallizes in a chiral space group, the lack of a significant anomalous scatterer makes determination of the absolute configuration impossible. Therefore, a random choice was made to refine the model having an R configuration at C3. After all nonhydrogen shift/esd ratios were less than 0.3, convergence was reached at the agreement factors listed in Table 4. No unusually high correlations were noted between any of the variables in the last cycle of the full-matrix least squares refinement, and the final difference density map showed a maximum peak of about 0.2 e Å^{-3}. All calculations were made using Nicolet's SHELXTL PLUS (1987) series of crystallographic programs.

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References

1) For reviews, see: a) W. J. De Klein, "Reactions with Manganese(III) Acetate," in "Organic Syntheses by Oxidation with Metal Compounds," ed by W. J. Mijs and C. R. H. I. De Jonge, Plenum, New York (1986), pp. 261—314. b) D. Arndt, "Manganese Compounds as Oxidizing Agents in Organic Chemistry," Open Court, La Salle (1981), pp. 1—25.

2) For intermolecular cyclization, see: a) N. Ito, H. Nishino, and K. Kurosawa, *Bull. Chem. Soc. Jpn.*, **56**, 3527 (1983). b) H. Nishino, *ibid.*, **58**, 217 (1985). c) W. E. Fristad and S. S. Hershberger, *J. Org. Chem.*, **50**, 1026 (1985). d) W. E. Fristad, J. R. Peterson, and A. B. Ernst, *ibid.*, **50**, 3143 (1985). e) E. J. Corey and A. W. Gross, *Tetrahedron Lett.*, **26**, 4291 (1985). f) N. Fujimoto, H. Nishino, and K. Kurosawa, *Bull. Chem. Soc. Jpn.*, **59**, 3161 (1986). g) H. Sato, H. Nishino, and K. Kurosawa, *ibid.*, **60**, 1753 (1987). h) E. J. Corey and A. K. Ghosh, *Tetrahedron Lett.*, **28**, 175 (1987); *Chem. Lett.*, **1987**, 223. i) F. Z. Yang, M. K. Trost, and W. E. Fristad, *Tetrahedron Lett.*, **28**, 1493 (1987). j) P. Breuilles and D. Uguen, *ibid.*, **31**, 357 (1990).

3) For intramolecular cyclization, see: a) E. J. Corey and M. Kang, *J. Am. Chem. Soc.*, **106**, 5384 (1984). b) B. B. Snider, R. Mohan, and S. A. Kates, *J. Org. Chem.*, **50**, 3661 (1985). c) A. B. Ernst and W. E. Fristad, *Tetrahedron Lett.*, **26**, 3761 (1985). d) B. B. Snider, R. Mohan, and S. A. Kates, *ibid.*, **28**, 841 (1987). e) R. Mohan, S. A. Kates, M. A. Dombroski, and B. B. Snider, *ibid.*, **28**, 845 (1987). f) B. B. Snider and M. A. Dombroski, *J. Org. Chem.*, **52**, 5487 (1987). g) J. R. Peterson, R. S. Egler, D. B. Horsley, and T. J. Winter, *Tetrahedron Lett.*, **28**, 6109 (1987). h) B. B. Snider, J. J. Patricia, and S. A. Kates, *J. Org. Chem.*, **53**, 2137 (1988). i) B. B. Snider and J. J. Patricia, *ibid.*, **54**, 38 (1989). j) A. Citterio, D. Fancelli, C. Finzi, and L. Pesce, *ibid.*, **54**, 2713 (1989). k) H. Oumar-Mahamat, C. Moustrou, J.-M. Surzur, and M. P. Bertrand, *ibid.*, **54**, 5684 (1989). l) J. D. White, T. C. Somers, and K. M. Yager, *Tetrahedron Lett.*, **31**, 59 (1990). m) S. A. Kates, M. A. Dombroski, and B. B. Snider, *J. Org. Chem.*, **55**, 2427 (1990).

4) a) E. I. Heiba, R. M. Desau, and W. J. Koehl, Jr., *J. Am. Chem. Soc.*, **91**, 138 (1969). b) H. Nishino and K. Kurosawa, *Bull. Chem. Soc. Jpn.*, **56**, 474 (1983). c) W. E. Fristad and J. R. Peterson, *J. Org. Chem.*, **50**, 10 (1985). d) H. Nishino, *Bull. Chem. Soc. Jpn.*, **59**, 1733 (1986). e) W. E. Fristad, J. R. Peterson, A. B. Ernst, and G. B. Urbi, *Tetrahedron*, **42**, 3429 (1986). f) A. Citterio and D. Fancelli, *Gazz. Chim. Ital.*, **118**, 405 (1988). g) A. Citterio, R. Santi, T. Fiorani, and S. Strologo, *J. Org. Chem.*, **54**, 2703 (1989). h) H. Nishino, K. Tsunoda, and K. Kurosawa, *Bull. Chem. Soc. Jpn.*, **62**, 545 (1989).

5) H. Nishino, *Bull. Chem. Soc. Jpn.*, **58**, 1922 (1985).

6) a) K. Kondo and M. Matsumoto, *J. Chem. Soc., Chem. Commun.*, **1972**, 1332. b) R. W. Denny and A. Nickon, *Org. React.*, **20**, 133. c) R. M. Wilson, E. J. Gardner, R. C. Eider, R. H. Squire, and L. R. Florian, *J. Am. Chem. Soc.*, **96**, 2955 (1974). d) M. Suzuki, H. Ohtake, Y. Kameya, M. Hamanaka, and R. Noyori, *J. Org. Chem.*, **54**, 5292 (1989), and references cited therein. e) S. Patai, "The Chemistry of Peroxides," John Wiley & Sons, New York (1983).

7) a) J. Yoshida, K. Sakaguchi, and S. Isoe, *Tetrahedron Lett.*, **28**, 667 (1987). b) J. Yoshida, S. Nakatani, K. Sakaguchi, and S. Isoe, *J. Org. Chem.*, **54**, 3383 (1989). c) J. Yoshida, S. Nakatani, and S. Isoe, *Tetrahedron Lett.*, **31**, 2425 (1990).

8) For preliminary report, see: S. Tategami, T. Yamada, H. Nishino, J. D. Korp, and K. Kurosawa, *Tetrahedron Lett.*,

31, 6371 (1990).

9) J. I. G. Cadogan and R. K. Mackie, *Chem. Soc. Rev.*, **3**, 87 (1974).

10) Crystallographic data of cyclic peroxides are available in Ref. 6d, and also: M. Sterns *J. Cryst. Mol. Struct.*, **1**, 373 (1971); A. Takenaka, Y. Sasada, and H. Yamamoto, *Acta Crystallogr., Sect. B*, **33**, 3566 (1977).

11) M. G. Vinogradov, Z. V. Todres, G. P. Il'ina, A. Rutavicius, D. N. Kursanov, and G. I. Nikishin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1976**, 1331.

12) J. B. Bush, Jr. and H. Finkbeiner, *J. Am. Chem. Soc.*, **90**, 5903 (1968); E. I. Heiba, R. M. Dessau, and W. J. Koehl, Jr., *ibid.*, **90**, 5905 (1968).

13) a) A. F. Nikolaev, K. V. Belogorodskaya, V. G. Shibalovich, E. D. Andreeva, L. V. Bogdanova, and M. V. Vinogradov, *Zh. Prikl. Khim. (Leningrad)*, **46**, 2718 (1973). b) A. F. Nikolaev, K. V. Belogorodskaya, V. G. Shibalovich, E. D. Andreeva, and G. I. Ivanova, *ibid.*, **48**, 2028 (1975). c) A. F. Nikolaev, K. V. Belogorodskaya, L. I. Pushkareeva, and E. D. Andreeva, *ibid.*, **49**, 937 (1976). d) K. V. Belogorodskaya, A. F. Nikolaev, V. G. Shibalovich, and L. I. Pushkareeva, *Vysokomol. Soedin., Ser. B*, **22**, 449 (1980); *Chem. Abstr.*, **93**, 221131r (1980).

14) a) T. Tsuruta, T. Harada, H. Nishino, and K. Kurosawa, *Bull. Chem. Soc. Jpn.*, **58**, 142 (1985). b) H. Yonemura, H. Nishino, and K. Kurosawa, *ibid.*, **59**, 3153 (1986).

15) a) M. Okano, T. Kinoshita, Y. Muramoto, and T. Aratani, *Nippon Kagaku Kaishi*, **1978**, 578. b) K. D. Donnelly, W. E. Fristad, B. J. Gellerman, R. J. Peterson, and B. J. Selle, *Tetrahedron Lett.*, **25**, 607 (1984).

16) a) W. D. Crow, W. Nicholls, and M. Sterns, *Tetrahedron Lett.*, **12**, 1353 (1971). b) M. L. Bolte, W. D. Crow, and S. Yoshida, *Aust. J. Chem.*, **35**, 1411, 1421, 1431 (1982).

17) Biological activity tests were performed by Sumitomo Chemical Co., Inc., Takarazuka, Hyogo, Japan.

18) M. N. Bhattacharjee, M. K. Chaudhuri, and D. T. Khathing, *J. Chem. Soc., Dalton Trans.*, **1982**, 669.

19) C. S. Marvel and W. M. Sperry, *Org. Synth.*, Coll. Vol. 1, 95 (1967).

20) W. S. Jonson, J. W. Petersen, and W. P. Schneider, *J. Am. Chem. Soc.*, **69**, 74 (1947).

21) W. A. Bonner and F. D. Mango, *J. Org. Chem.*, **29**, 430 (1964).

22) H. Stetter and M. Schreckenberg, *Chem. Ber.*, **107**, 2453 (1974).

23) O. G. Backeberg and J. L. Marais, *J. Chem. Soc.*, **1945**, 803.

24) W. T. Nauta, M. J. Ernsting, and A. C. Faber, *Recl. Trav. Chim. Pays-Bas*, **60**, 915 (1941).

25) G. E. Moussa, M. N. Basyouni, and M. E. Shaben, *Indian J. Chem., Sect. B*, **19**, 800 (1980).

26) J. H. Helberger, *Liebigs Ann. Chem.*, **522**, 269 (1936).

27) D. Seyferth and R. J. Spohn, *J. Am. Chem. Soc.*, **90**, 540 (1968).

28) E. I. Heiba and R. M. Dessau, *J. Org. Chem.*, **23**, 3456 (1974).

29) Benzene (Wako) was treated with concd. H_2SO_4, washed with water, aqueous Na_2CO_3 and then with water, dried over anhydrous $CaCl_2$, and distilled from sodium diphenylketyl. Petroleum ether (Nacalai) was extracted with concd H_2SO_4 three times and then with $KMnO_4$–10% H_2SO_4 aqueous solution, washed with water, aqueous Na_2CO_3 and then with water, dried over anhydrous $CaCl_2$, and distilled. The distilled benzene and petroleum ether were stored under argon.

30) N. Staudinger and E. Hauser, *Helv. Chim. Acta*, **4**, 861 (1921).

31) W. Borsche and W. Menz, *Ber.*, **41**, 190 (1908).

32) E. P. Kohler and H. Engelbrecht, *J. Am. Chem. Soc.*, **41**, 764 (1919).

33) Tables 2—8 containing X-ray crystallographic data consisting of atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, H-atom coordinates and isotropic displacement parameters, hydrogen bonding parameters, and torsion angles for **3a** (7 pages); and Table 9 containing observed and calculated structure factors (8 pages) are deposited as Document No. 9115 at the Office of the Editor of Bull. Chem. Soc. Jpn.