Manganese(III) or Cobalt(III)-Mediated Oxidative Radical Reactions of Terminal Dienes. One-Pot Synthesis of Bis(dihydrofuran)s

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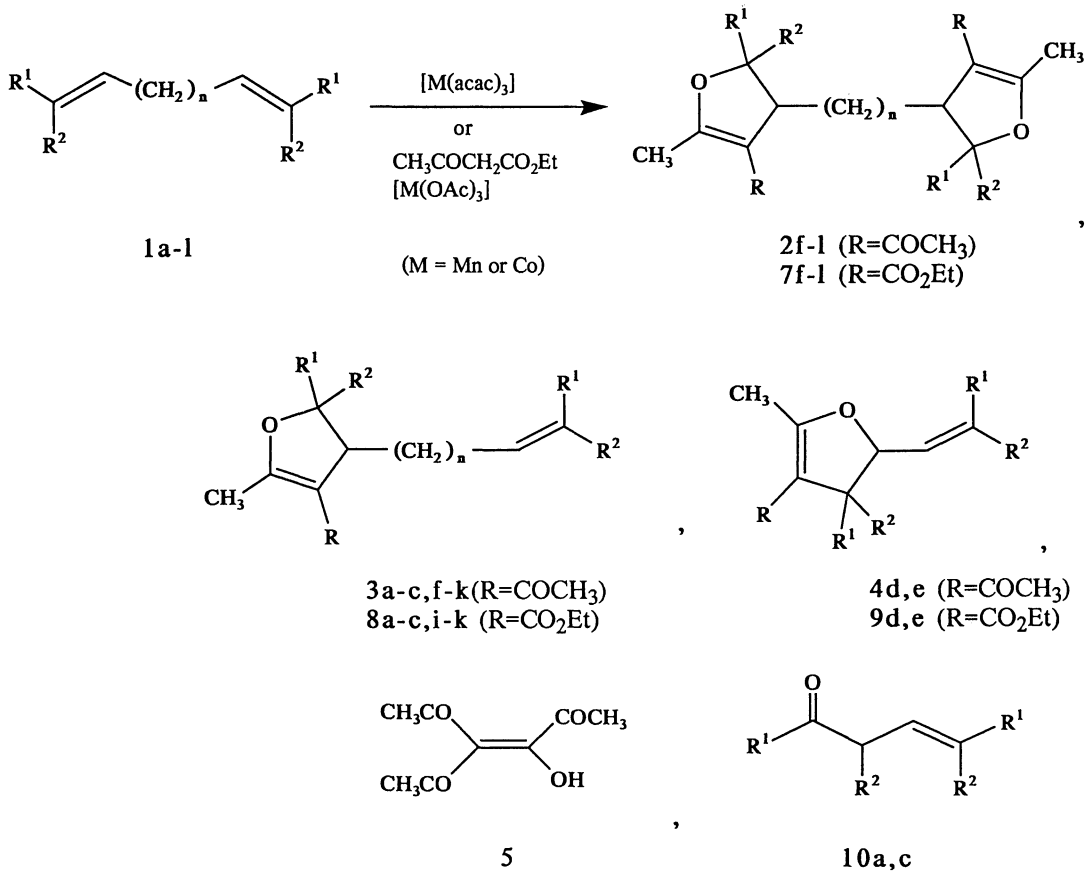
(Received October 31, 1990)

The reactions of terminal dienes such as 1,4-pentadienes and 1,5-hexadienes with tris(2,4-pentanedionato)-manganese(III) ([Mn(acac)$_3$]) gave α,ω-bis(dihydrofuryl)alkanes (abbreviated bis(dihydrofuran)s, hereafter) in good yields. The reactions with tris(2,4-pentanedionato)cobalt(III) ([Co(acac)$_3$]) instead of [Mn(acac)$_3$] yielded the same bis(dihydrofuran)s quantitatively. The dienes also reacted with ethyl 3-oxobutanoate in the presence of manganese(III) acetate ([Mn(OAc)$_3$]) or cobalt(IlI) acetate ([Co(OAc)$_3$]) to produce the corresponding bis(dihydrofuran)s. The reactions of 1,3-butadienes with the manganese(III) or cobalt(III) complexes afforded only mono(dihydrofuran)s and oxidative rearrangement products, but the corresponding bis(dihydrofuran)s were not formed. The reaction of 1,5-hexadienes with ethyl hydrogen malonate in the presence of [Mn(OAc)$_3$] did not give bis-annulated products, but mono(γ-lactone)s in moderate yields. The synthetic applications and limitations of the bis(dihydrofuran)s formation are discussed.

Recently, one of the most interesting synthetic methods in organic chemistry was reported. That is the technique involving the intermolecular or intramolecular cyclization reaction of alkenes or alkynes using metal compounds, such as palladium, nickel, cobalt, ruthenium, manganese, chromium, and so on.[1] Especially, we are very interested in the intermolecular or intramolecular radical cyclization reaction using manganese(III) or cobalt(III) complexes.[1c] Previously we reported the oxidation of alkenes with malonic acid in the presence of manganese(III) acetate[2] which was simply abbreviated [Mn(OAc)$_3$].[3] This reaction gave 2,7-dioxaspiro[4.4]nonane-1,6-diones in high yields, although we could not control their stereochemistry at the C-3 and C-8 carbons. Similar reactions with malonic acid derivatives, such as methylmalonic acid, bromomalonic acid, chloromalonic acid, and ethyl hydrogen malonate, yielded the corresponding 2-carboxy-4-butanolides and/or 2-buten-4-olides in good yields.[5] Using malonamide or 2-cyanoacetamide instead of malonic acid in these oxidation reactions afforded not only 2-buten-4-olides, but also 1,5-dihydro-2*H*-pyrrol-2-ones in moderate yields.[6,7] Fristad,[8] Snider,[9] Corey,[10] and Citterio[11] also reported the manganese(III)-mediated inter- or intra-molecular radical cyclization reactions. In connection with the oxidative inter- or intramolecular cyclization reaction using [Mn(OAc)$_3$], we noticed that the ligand-exchange reaction of the manganese(III) complex occurred easily in acetic acid and the corresponding ligand radicals were readily formed.[12] Then, we discovered the facile synthesis of dihydrofurans using tris(2,4-pentanedionato)-manganese(III) ([Mn(acac)$_3$]).[12a] It was also shown that tris(2,4-pentanedionato)cobalt(III) ([Co(acac)$_3$]) had a similar role in acetic acid.[12c] Heiba and Dessau reported that the reaction of styrene with ethyl 3-oxobutanoate in the presence of [Mn(OAc)$_3$] also gave the corresponding dihydrofuran in 57% yield.[13] Corey applied these methods to enol ethers and obtained 2-alkoxy-2,3-dihydrofurans which were transformed to fused or spiro 2-cyclopentenones or converted to the corresponding furans in good yields.[14] However, any attempts to get α,ω-bis(dihydrofuryl)alkanes (abbreviated bis(dihydrofuran)s, hereafter), which might have either an antibiotic nature or bioactive character[15] or might be used as a starting material for the synthesis of many kinds of natural products containing furan rings,[16] were not accomplished by taking advantage of the ligand-exchange process of the manganese(III) or cobalt(III) complexes. We describe in this paper the one-pot synthesis of bis(dihydrofuran)s using Mn(III)- or Co(III)-promoted annulation.

Results

Reaction of Dienes with [Mn(acac)$_3$] or [Co(acac)$_3$]. We used 1,3-butadienes (**1a—e**), 1,4-pentadienes (**1f—h**), and 1,5-hexadienes (**1i—l**) as a substrate (Fig. 1). The reaction of **1a** with [Mn(acac)$_3$] was carried out in the molar ratio from 1 : 4 to 1 : 10 in boiling acetic acid until the oxidant was consumed completely, which gave only 4-ethenyl-4,5-dihydrofuran (**3a**) and 3-acetyl-4-hydroxy-3-hexene-2,5-dione (**5**) in the yields shown in Table 1. An expected bis(dihydrofuran), however, was not formed. The reaction of **1b—e** with [Mn(acac)$_3$] also gave only mono(dihydrofuran)s (**3b,c** and **4d,e**) and the dione (**5**). The results for the reaction of **1d** and **1e** were similar to Hanafusa's work.[17] The 1,4-pentadiene (**1f**) reacted with [Mn(acac)$_3$] to afford the expected bis(dihydrofuran) (**2f**) in moderate yield, although mono(dihydrofuran) (**3f**) was also formed together with **2f** in the reaction at a lower oxidant/substrate ratio (Table 1, Entry 11). The same type of products were obtained from the reactions of **1g** and **1h** (Table 1, Entries 14 and 16). Similar reactions of 1,5-hexadienes (**1i—l**) with



a : n=0, R^1=R^2=Ph
b : n=0, R^1=R^2=4-ClC_6H_4
c : n=0, R^1=R^2=4-MeC_6H_4
d : n=0, R^1=Ph, R^2=H
e : n=0, R^1=R^2=Me
f : n=1, R^1=R^2=Ph
g : n=1, R^1=R^2=4-ClC_6H_4
h : n=1, R^1=R^2=4-MeC_6H_4
i : n=2, R^1=R^2=Ph
j : n=2, R^1=R^2=4-ClC_6H_4
k : n=2, R^1=R^2=4-MeC_6H_4
l : n=2, R^1=R^2=4-$MeOC_6H_4$

Fig. 1.

[Mn(acac)3] gave the expected bis(dihydrofuran)s (**2i—k**) in good yields except for **21** (Table 1).

The reaction using [Co(acac)3] instead of [Mn(acac)3] resulted in an increased yield of the bis(dihydrofuran). Especially, bis(dihydrofuran)s (**2i—l**) were obtained quantitatively. However, the yield of mono(dihydrofuran)s (**3a—c**, **4e**) was not improved in the oxidation of **1a—e**.

Reaction of Dienes with Ethyl 3-Oxobutanoate in the Presence of Manganese(III) Acetate or Cobalt(III) Acetate. The dienes (**1a—l**) were oxidized with [Mn(OAc)3] in the presence of ethyl 3-oxobutanoate under various reaction conditions. The results are shown in Table 2. When **1f—l** were used during this reaction, the corresponding bis(dihydrofuran)s (**7f—l**) were produced in good to moderate yields. However, we could not obtain any bis(dihydrofuran)s in the case of 1,3-butadienes (**1a—e**), but only ethenyl-substituted dihydrofurans (**8a—c**, and **9d,e**) together with oxidative rearrangement products (**10a,c**). On the other hand, the reaction of 1,5-hexadienes (**1i—l**) with cobalt(III) acetate ([Co(OAc)3])[18] gave both bis(dihydrofuran)s (**7i—l**) and mono(dihydrofuran)s (**8i—k**). The product yields of the reactions by [Co(OAc)3], however, were lower than those of the reactions employing [Mn(OAc)3].

Reactions of 1,5-Hexadienes (1i—l) with Ethyl Hydrogen Malonate in the Presence of [Mn(OAc)3]. It was reported that the reaction of 1-heptene with diethyl malonate in the presence of [Mn(OAc)3]/[Cu(OAc)2] afforded heptylmalonate.[20] However, intramolecular cyclization did not occur under the reaction conditions. Fristad examined the reaction of 1,5-hexadienes with malonic acid and obtained 2,7-dioxacyclopenta[*c*]pentalene-1,8-diones in low yields.[8a] So the reaction of **1i—l** with ethyl hydrogen malonate in the presence of [Mn(OAc)3] was examined in order to get bis-annulated lactone and compare this

Table 1. Reaction of Terminal Dienes (**1a—l**) with [M(acac)$_3$] (M=Mn, Co) in Boiling Acetic Acid

Entry	Diene	Oxidant	Molar ratio[a]	Reaction time[b] / min	Product (yield/%)[c]				Recovered diene / %
1	**1a**	[Mn(acac)$_3$]	1:4	2		**3a**(19)		**5**(42)	78
2			1:10	3		**3a**(35)		**5**(46)	56
3		[Co(acac)$_3$]	1:6	120		**3a**(42)			56
4	**1b**	[Mn(acac)$_3$]	1:10	2		**3b**(30)		**5**(48)	69
5		[Co(acac)$_3$]	1:6	120		**3b**(21)			73
6	**1c**	[Mn(acac)$_3$]	1:6	2		**3c**(38)		**5**(40)	36
7		[Co(acac)$_3$]	1:6	120		**3c**(56)			26
8	**1d**	[Mn(acac)$_3$]	1:2	1			**4d**(85)		6
9	**1e**	[Mn(acac)$_3$]	1:8	2			**4e**(72)	**5**(33)	
10		[Co(acac)$_3$]	1:1	42			**4e**(20)		
11	**1f**	[Mn(acac)$_3$]	1:4	1	**2f**(13)	**3f**(12)		**5**(17)	
12			1:10	2	**2f**(48)			**5**(22)	
13		[Co(acac)$_3$]	1:10	150	**2f**(70)				
14	**1g**	[Mn(acac)$_3$]	1:10	2	**2g**(23)	**3g**(22)		**5**(29)	24
15		[Co(acac)$_3$]	1:10	150	**2g**(47)				
16	**1h**	[Mn(acac)$_3$]	1:8	2	**2h**(71)	**3h**(11)		**5**(25)	
17		[Co(acac)$_3$]	1:10	150	**2h**(78)	**3h**(18)			
18	**1i**	[Mn(acac)$_3$]	1:10	3	**2i**(71)	**3i**(17)		**5**(31)	4
19		[Co(acac)$_3$]	1:6	90	**2i**(92)				
20	**1j**	[Mn(acac)$_3$]	1:10	2	**2j**(46)	**3j**(24)		**5**(28)	16
21		[Co(acac)$_3$]	1:10	150	**2j**(91)				
22	**1k**	[Mn(acac)$_3$]	1:2	1	**2k**(29)	**3k**(39)			30
23			1:10	2	**2k**(98)				
24		[Co(acac)$_3$]	1:10	150	**2k**(92)				
25	**1l**	[Mn(acac)$_3$]	1:8	2	**2l**(29)			**5**(15) **6**(45)	
26		[Co(acac)$_3$]	1:10	150	**2l**(91)				

a) Diene: [M(acac)$_3$]. b) The reaction time shows consumption time of each oxidant. c) The yield based on the diene added except for the yield of product (**5**) which was calculated by [Mn(acac)$_3$] added.

Table 2. Reactions of Terminal Dienes (**1a—l**) with Ethyl 3-Oxobutanoate in the Presence of [M(OAc)$_3$] (M=Mn, Co)[a]

Entry	Diene	Oxidant	Molar ratio[b]	Reaction time[c] / min	Product (yield/%)[d]				
1	**1a**	[Mn(OAc)$_3$]	1:4:6	5			**8a**(46)		**10a**(12)
2[e]	**1b**		1:4:6	7			**8b**(29)		
3	**1c**		1:2:4	3			**8c**(11)		**10c**(72)
4[f]	**1d**		1:1:2	1				**9d**(49)	
5	**1e**		1:2:4	4				**9e**(57)	
6	**1f**		1:4:6	4		**7f**(22)			
7	**1g**		1:6:8	8		**7g**(17)			
8	**1h**		1:6:8	8		**7h**(14)			
9	**1i**		1:6:8	6		**7i**(89)			
10		[Co(OAc)$_3$]	1:6:8	180		**7i**(61)	**8i**(38)		
11	**1j**	[Mn(OAc)$_3$]	1:6:8	4		**7j**(71)			
12		[Co(OAc)$_3$]	1:6:8	150		**7j**(43)	**8j**(50)		
13	**1k**	[Mn(OAc)$_3$]	1:5:7	9		**7k**(79)			
14		[Co(OAc)$_3$]	1:6:8	90		**7k**(69)	**8k**(23)		
15	**1l**	[Mn(OAc)$_3$]	1:5:7	4	**6**(11)	**7l**(62)			
16		[Co(OAc)$_3$]	1:6:8	120		**7l**(trace)			

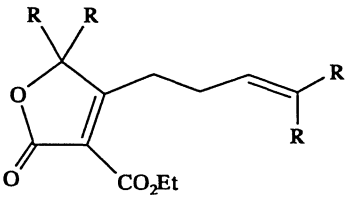
a) The reactions were carried out in acetic acid at reflux temperature until the each oxidant was consumed completely. b) Diene: $CH_3COCH_2CO_2Et$: [M(OAc)$_3$]. c) The reaction time shows consumption time of each oxidant. d) The yield based on the diene added. e) The diene (**1b**) was recovered (14%). f) The diene (**1d**) was recovered (17%).

reaction with the bis(dihydrofuran) formation reaction previously mentioned. The 1,5-hexadienes (**1i—l**) and ethyl hydrogen malonate were oxidized with [Mn(OAc)$_3$] in boiling acetic acid to yield 3-(3-butenyl)-2-buten-4-olides (**11i—l**). The results are shown in Table 3.

Table 3. Reactions of Terminal Dienes (**1i—l**) with Ethyl Hydrogen Malonate in the Presence of $[Mn(OAc)_3]$[a)]

Entry	Diene	Molar ratio[b)]	Reaction time[c)] / min	Product (yield/%)[d)]	Recovered diene / %
1	**1i**	1:4:5	1	**11i**(81)	11
2	**1j**	1:4:5	2	**11j**(65)	
3	**1k**	1:4:5	6	**11k**(47)	9
4	**1l**	1:6:7	1	**11l**(33)	

a) The reactions were carried out in acetic acid at reflux temperature until the oxidant was consumed completely. b) Diene: Ethyl hydrogen malonate: $[Mn(OAc)_3]$. c) The reaction time shows consumption time of the oxidant. d) The yield based on the diene added.



11i-l

i : R=Ph
j : R=4-ClC_6H_4
k: R=4-MeC_6H_4
l : R=4-$MeOC_6H_4$

Fig. 2.

Discussion

We reported the reaction mechanism for the formation of the dihydrofuran ring involving diacetylmethyl radical, $\cdot CH(COCH_3)_2$, which was produced by the thermolysis of $[Mn(acac)_3]$ or $[Co(acac)_3]$ in boiling acetic acid.[12a)] Therefore, the formation of bis(dihydrofuran)s (**2f—l**) using $[Mn(acac)_3]$ or $[Co(acac)_3]$ could be also explained by an akin mechanism previously discussed. The reactions of 1,4-pentadienes (**1f—h**) and 1,5-hexadienes (**1i—l**) with $[Mn(acac)_3]$ or $[Co(acac)_3]$ gave expected **2f—l** in good yields. However, it was very difficult to get the corresponding bis(dihydrofuran)s by the reaction of 1,3-butadienes (**1a—e**), and considerable amounts of **1a—c** were recovered even for the reactions at a high oxidant/substrate ratio after completion of the reaction. This was considered to be due to the bulky diacetylmethyl radicals not being able to attack the other sterically crowded double bond after forming one dihydrofuran ring in the 1,3-butadiene molecule, because **1a—c** have two pairs of aryl groups at the terminal carbons and the carbon chain (n=0) was very short. Therefore, only mono(dihydrofuran)s (**3a—c** and **4d,e**) were obtained from the reaction of **1a—e**. The generation of isomeric ring systems of **3a—c** and **4d,e** is due to the stability of the intermediate radical (**I** and **II**), that is to say, the benzyl type radical **I** formed from **1a—c** was stabilized by two aryl groups (R^1=R^2=aryl) and the allyl type radical **II** produced from **1d** and **1e** was stabilized by allyl conjugation (Fig. 3). For the reaction of 1,4-pentadienes (**1f—h**) using $[Co(acac)_3]$ the yield of **2f—h** was slightly better than that using $[Mn(acac)_3]$. However, the yield of **2g** was low in both cases since the corresponding benzyl radical, e.g., radical **I** was destabilazed by the inductive effect of chloro-substituent on the aryl ring. The reaction of 1,5-hexadienes (**1i—l**) with $[Co(acac)_3]$ gave **2i—l** quantitatively and no effect of substituents was

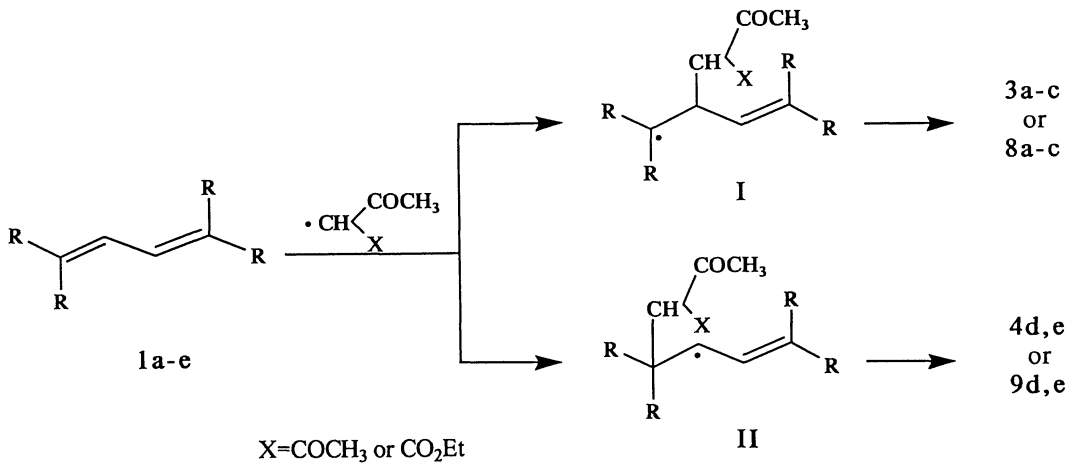
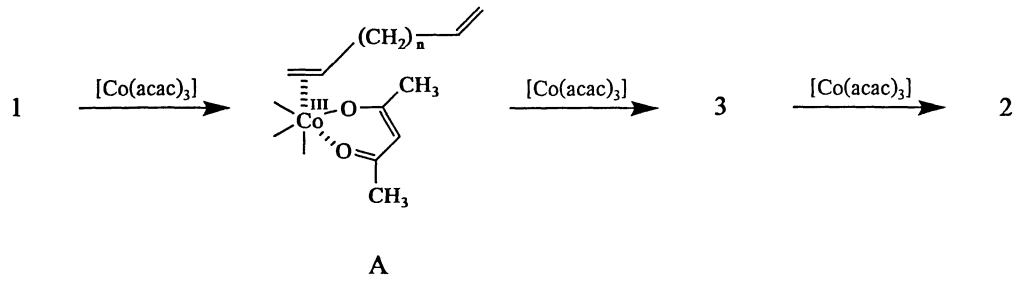


Fig. 3.

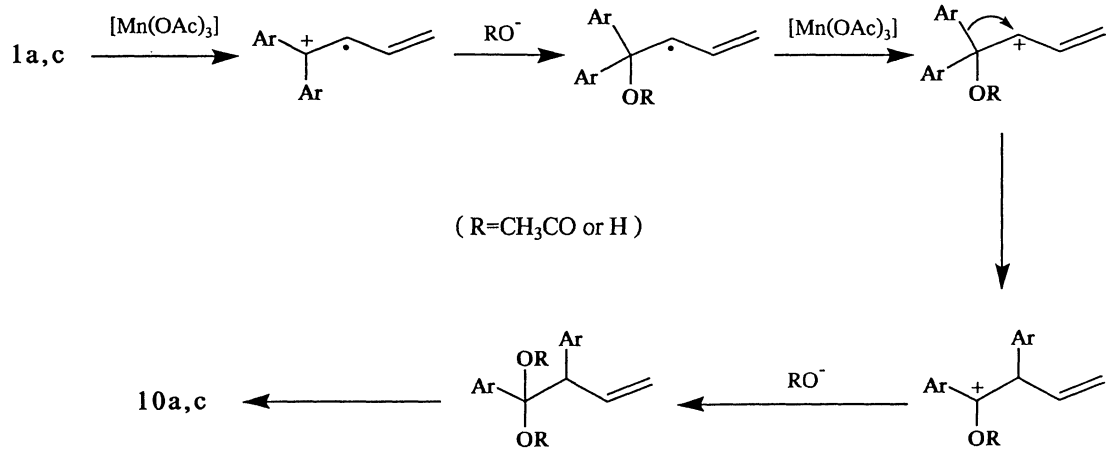
observed. On the other hand, **2l** was obtained in poor yield when [Mn(acac)3] was used. This result clearly showed that the electron-transfer from **1l** to Mn(III), generally observed during the oxidation with metal compounds,[1c,21] occurred predominantly since the electron-donating effect of the methoxyl group on the aromatic ring lowered the ionization potential of **1l**.[6,22-24] Actually 4,4′-dimethoxybenzophenone (**6**), which was a typical product via the electron-transfer reaction process, was obtained as the main product (Table 1, Entry 25).

In order to explain the fact that [Co(acac)3] was superior to [Mn(acac)3] for the formation of dihydrofuran ring, we propose the mechanism via the complex formation between [Co(acac)3] and diene. The nature of the complex could be either π- or σ-complex,[25-28] but it is not clear at present moment. Then the oxidation of the complex (**A**) with Co(III) would give rise to mono(dihydrofuran) (**3**). The similar reaction of **3** with [Co(acac)3] was repeated to yield bis(dihydrofuran) (**2**). The reaction mechanism is briefly shown in Scheme 1. On the other hand, it was considered that [Mn(acac)3] could not make a complex (e.g., either π-complex or σ-complex) with the terminal diene or the interaction between [Mn(acac)3] and the diene was very weak. Accordingly, the diacetylmethyl radical has roughly two chances for coupling reactions; one is the coupling between the diene and diacetylmethyl radical and the other is a bimolecular radical coupling of the diacetylmethyl radical itself. In fact, the by-product (**5**), which is usually formed in the [Mn(acac)3]-AcOH oxidation system, was obtained in all of the reactions with [Mn(acac)3] regardless of these substrates.[22] The formation mechanism of **5** via the bimolecular radical coupling of diacetylmethyl radical will be discussed elsewhere.[12c]

Similar results for the synthesis of bis(dihydrofuran)s were obtained by the reaction of dienes (**1a—l**) with ethyl 3-oxobutanoate in the presence of [Mn(OAc)3] or [Co(OAc)3]. In the case of **1i—l**, however, the product yields using [Co(OAc)3] were lower than those using [Mn(OAc)3]. This can be ascribed to the different behavior of [Mn(OAc)3] and [Co(OAc)3] in the reaction system. In other words, if ethyl 3-oxobutanoate radical, $\cdot CH(COCH_3)CO_2Et$, is formed during the ligand-exchange reaction between metal acetate and the oxobutanoate,[8a,29] the ligand-exchange reaction between [Mn(OAc)3] and the oxobutanoate must be much faster than that between [Co(OAc)3] and the oxobutanoate. Therefore, the reaction of **1i—l** in the presence of [Mn(OAc)3] gave the corresponding bis(dihydrofuran)s (**7i—l**) in good yields for much shorter reaction time (4—9 min). On the other hand, it must need much longer reaction time (90—180 min) for the consumption of



Scheme 1.



Scheme 2.

[$Co(OAc)_3$] since the ligand-exchange reaction between [$Co(OAc)_3$] and the oxobutanoate is much slower, although Co(III) is a stronger oxidant than Mn(III) according to the comparison with the standard potential ($E°$) of single electrode.[30] Thus, it is considered that the yields of **7i—l** are lower than those using [$Mn(OAc)_3$] since the ligand-exchange reaction between [$Co(OAc)_3$] and the oxobutanoate competes with other side-reactions such as oxidative decarboxylation of solvent.[31] It is noteworthy that the reactions of **1a** and **1c** with [$Mn(OAc)_3$] gave oxidative rearrangement products (**10a** and **10c**) along with mono(dihydrofuran)s (**8a** and **8c**). This rearrangement is presumed to occur via the oxidation through the electron-transfer process regardless of the presence of ethyl 3-oxobutanoate (Scheme 2). Furthermore, it was confirmed that the rearrangement occurred intramolecularly according to the result for the cross-over experiment (see Experimental).

It is not clear why no bis-annulated compound was formed in the reaction with ethyl hydrogen malonate. Even if the molar ratio of **1i**:ethyl hydrogen malonate:[$Mn(OAc)_3$] was increased up to 1:6:7, the corresponding bis-annulated lactone was not isolated and an intractable mixture was obtained (see Experimental). Probably, **11i** was simply oxidized with [$Mn(OAc)_3$] to give a complex mixture before the second attack of $\cdot CH(CO_2Et)CO_2H$ radical to **11i**, or ethyl hydrogen malonate itself was also oxidized to decomposition (the decomposed products were not checked).

In conclusion, [$Co(acac)_3$] has a higher selectivity for the formation of bis(dihydrofuran)s than [$Mn(acac)_3$]. [$Mn(OAc)_3$] is better than [$Co(OAc)_3$] for the production of bis(dihydrofuran)s in the presence of ethyl 3-oxobutanoate under present reaction conditions. In addition, the terminal dienes, which have longer carbon chains than 1,3-butadienes, are advantageous for the synthesis of bis-annulated compounds. We firmly believe that the synthesis of bis(dihydrofuran)s utilizing the present method is important since bis(dihydrofuran)s can be converted to the corresponding bis(furan)s and bis(tetrahydrofuran)s.

Experimental

Instrumentation. ^1H NMR spectra were measured in chloroform-*d* on either a JEOL JNM-PMX60SI or a JEOL FX90Q spectrometer. Chemical shifts are reported in ppm downfield from an intermal TMS standard. Infrared spectra were recorded in chloroform on a JASCO A-102 infrared spectrometer. The IR spectral data are expressed in cm^{-1}. Mass spectra were measured on either a JEOL JMS-01SG-2, JMS-DX303HF, or a Finnigan 6000 GC/MS mass spectrometer at 70 eV of ionization energy. All melting points were determined with a Yanaco MP-J3 micromelting point apparatus (Yanagimoto) and were uncorrected. Elemental analyses were performed by the Elemental Analysis Center, Faculty of Science, Kyushu University.

Materials. Tris(2,4-pentanedionato)manganese(III),[32] manganese(III) acetate,[33] and cobalt(III) acetate[19] were prepared according to methods previously described. Tris(2,4-pentanedionato)cobalt(III) (Wako) was used as received. 1,3-Butadienes (**1a—c**) were prepared by dehydration of the corresponding diols which were synthesized from diethyl succinate (Nacalai) and the corresponding phenylmagnesium bromide. 1,1,4,4-Tetraphenyl-1,3-butadiene (**1a**): Yellow microcrystals (from benzene), mp 195—197 °C (lit,[34] mp 192—193 °C). 1,1,4,4-Tetrakis(4-chlorophenyl)-1,3-butadiene (**1b**): Yellow needles (from benzene), mp 240—242 °C (lit,[35] mp 244 °C). 1,1,4,4-Tetrakis(4-methylphenyl)-1,3-butadiene (**1c**): Pale yellow needles (from acetic acid), mp 251—253 °C (lit,[36] mp 248—250 °C). 1,4-Diphenyl-1,3-butadiene (**1d**) (Aldrich) and 2,5-dimethyl-2,4-hexadiene (**1e**) (Aldrich) were used as received. 1,4-Pentadienes (**1f—h**) were prepared from diethyl glutarate (Tokyokasei) and the corresponding phenylmagnesium bromide according to the similar reaction previously mentioned. 1,1,5,5-Tetraphenyl-1,4-pentadiene (**1f**): Orange liquid; IR 1656 (C=C); ^1H NMR δ=2.80—3.17 (2H, m, $-CH_2-$), 5.90—6.25 (2H, m, 2×=CH-), and 6.90—7.70 (20H, m, 4×Ph). 1,1,5,5-Tetrakis(4-chlorophenyl)-1,4-pentadiene (**1g**): Yellow liquid; IR 1650 (C=C); ^1H NMR δ=2.67—3.13 (2H, m, $-CH_2-$), 5.83—6.23 (2H, m, 2×=CH-), and 6.77—7.78 (16H, m, arom. H). 1,1,5,5-Tetrakis(4-methylphenyl)-1,4-pentadiene (**1h**): Pale yellow microcrystals (from benzene-petroleum ether), mp 94—96 °C; IR 1665 (C=C); ^1H NMR δ=2.30 (6H, s, 2×Me), 2.34 (6H, s, 2×Me), 2.78—3.13 (2H, m, $-CH_2-$), 5.88—6.22 (2H, m, 2×=CH-), and 6.93—7.22 (16H, m, arom.H). 1,1,6,6-Tetraphenyl-1,5-hexadiene (**1i**) was prepared from 1,4-dibromobutane (Wako) and benzophenone (Wako) according to the procedure previously described: Colorless needles (from ethyl acetate-ethanol), mp 101—102 °C (lit,[37] mp 108—109 °C). Other 1,5-hexadienes (**1j—l**) were prepared from diethyl adipate (Nacalai) and the corresponding phenylmagnesium bromide. 1,1,6,6-Tetrakis(4-chlorophenyl)-1,5-hexadiene (**1j**): Colorless microcrystals (from ethyl acetate-ethanol), mp 177—179 °C; IR 1669 (C=C); ^1H NMR δ=2.12—2.33 (4H, m, 2×$-CH_2-$), 5.83—6.20 (2H, m, 2×CH-), and 6.90—7.60 (16H, m, arom.H). 1,1,6,6-Tetrakis(4-methylphenyl)-1,5-hexadiene (**1k**): Colorless microcrystals (from benzene-hexane), mp 134—136 °C; IR 1660 (C=C); ^1H NMR δ=2.11—2.29 (4H, m, 2×$-CH_2-$), 2.31 (6H, s, 2×Me), 2.39 (6H, s, 2×Me), 5.94—6.23 (2H, m, 2×=CH-), and 6.91—7.58 (16H, m, arom.H). 1,1,6,6-Tetrakis(4-methoxyphenyl)-1,5-hexadiene (**1l**): Yellow-green needles (from ether), mp 106—107 °C (lit,[38] mp 108 °C). Ethyl 3-oxobutanoate (Wako) was used as received. Ethyl hydrogen malonate was prepared from diethyl malonate (Wako) according to the literature:[39] Colorless liquid, bp_{19} 145 °C (lit,[39] bp_{21} 147 °C).

Reaction of Terminal Dienes with [Mn(acac)$_3$]. The typical procedure for the reaction of terminal dienes with [$Mn(acac)_3$] was as follows. To a heated solution of a terminal diene (0.5—1.0 mmol) in acetic acid (30 cm^3), [$Mn(acac)_3$] was added. The mixture was heated under reflux until the opaque dark brown color turned a clear yellow. The solvent was removed in vacuo and the residue was triturated with 2M (1M=1 mol dm^{-3}) HCl (30 cm^3), followed by extraction with chloroform. The chloroform extract was concentrated and the residue was separated on TLC (either Wakogel B-10 or Kieselgel 60G) with chloro-

form as the developing solvent. The yields are summarized in Table 1.

Reaction Products. 3-Acetyl-2-methyl-4-(2,2-diphenylethenyl)-5,5-diphenyl-4,5-dihydrofuran (3a): Yellow liquid; IR 1662 (C=O); ^{1}H NMR δ=2.21 (3H, s, COMe), 2.37 (3H, s, Me), 4.81 (1H, d, J=11.0 Hz, >CH-), 5.44 (1H, d, J=11.0 Hz, =CH-), and 6.54—7.79 (20H, m, 4×Ph); MS m/z (rel intensity) 456 (M^+, 44), 414 (60), 289 (58), 231 (65), 215 (81), 165 (100), and 105 (50). Found: m/z 456.2098. Calcd for $C_{33}H_{28}O_2$: M, 456.2089.

3-Acetyl-4-[2,2-bis(4-chlorophenyl)ethenyl]-5,5-bis(4-chlorophenyl)-2-methyl-4,5-dihydrofuran (3b): Yellow liquid; IR 1664 (C=O); ^{1}H NMR δ=2.27 (3H, s, COMe), 2.38 (3H, s, Me), 4.75 (1H, d, J=11.0 Hz, >CH-), 5.37 (1H, d J=11.0 Hz, =CH-), and 6.47—7.57 (16H, m, arom.H); MS m/z (rel intensity) 594 (M^+, 34), 592 (M^+, 26), 552 (75), 550 (60), 534 (56), 532 (44), 357 (26), 315 (18), 299 (33), 277 (37), 264 (26), 251 (36), 235 (26), 199 (41), 165 (13), 139 (56), and 111 (12). Found: m/z 594.0499; 592.0529. Calcd for $C_{33}H_{24}O_2{}^{35}Cl_3{}^{37}Cl$; $C_{33}H_{24}O_2{}^{35}Cl_4$: M, 594.0506; 592.0530.

3-Acetyl-4-[2,2-bis(4-methylphenyl)ethenyl]-5,5-bis(4-methylphenyl)-2-methyl-4,5-dihydrofuran (3c): Yellow liquid; IR 1661 (C=O); ^{1}H NMR δ=2.18 (3H, s, Me), 2.22 (6H, s, 2×Me), 2.25 (3H, s, Me), 2.35 (3H, s, Me), 2.42 (3H, s, Me), 4.76 (1H, d, J=11.0 Hz, >CH-), 5.12 (1H, d, J=11.0 Hz, =CH-), and 6.51—7.40 (16H, m, arom.H); MS m/z (rel intensity) 512 (M^+, 55), 469 (100), 452 (96), 317 (31), 219 (32), and 195 (49). Found: m/z 512.2707. Calcd for $C_{37}H_{36}O_2$: M, 512.2715.

3-Acetyl-2-methyl-5-[(*E*)-2-phenylethenyl]-4-phenyl-4,5-dihydrofuran (4d): Colorless needles (from methanol), mp 101—103 °C; IR 1663 (C=O); ^{1}H NMR δ=1.86 (3H, s, COMe), 2.38 (3H, d, J=1.8 Hz, Me), 4.18 (1H, dq, J=6 and 1.8 Hz, H-4), 4.91 (1H, t, J=6 Hz, H-5), 6.23 (1H, dd, J=6 and 16 Hz, =CH-), 6.55 (1H, d, J=16 Hz, =CH-), and 6.85—7.55 (10H, m, arom.H). Found: C, 82.76; H, 6.57%. Calcd for $C_{21}H_{20}O_2$: C, 82.86; H, 6.57%.

3-Acetyl-5-(2-methyl-1-propenyl)-2,4,4-trimethyl-4,5-dihydrofuran (4e): Yellow liquid; IR 1655 (C=O); ^{1}H NMR δ=1.07 (3H, s, Me), 1.25 (3H, s, Me), 1.68 (3H, d, J=1.2 Hz, Me), 1.76 (3H, d, J=1.2 Hz, Me), 2.19 (3H, s, Me), 2.26 (3H, s, Me), 4.75 (1H, d, J=10 Hz, >CH-), and 5.38 (1H, br.d, J=10 Hz, =CH-); MS m/z (rel intensity) 209 (100), 208 (M^+, 9), 197 (6), 181 (36), 155 (13), 110 (10), and 83 (3). Found: m/z 208.1443. Calcd for $C_{13}H_{20}O_2$: M, 208.1463.

3-Acetyl-4-hydroxy-3-hexene-2,5-dione (5): Colorless prisms (from benzene), mp 113—114 °C (lit,[22] mp 115—116 °C).

Bis(4-acetyl-5-methyl-2,2-diphenyl-2,3-dihydro-3-furyl)-methane (2f): Yellow liquid; IR 1679 (C=O); ^{1}H NMR δ=1.65—1.76 (2H, m, -CH_2-), 2.12 (6H, s, 2×COMe), 2.18 (6H, s, 2×Me), 4.1 (2H, br.t, J=6 Hz, 2×>CH-), and 6.70—7.93 (20H, m, arom.H); MS m/z (rel intensity) 568 (M^+, 15), 468 (10), 401 (5), 290 (100), 277 (53), 235 (10), 191 (10), 167 (15), and 91 (8). Found: m/z 568.2626. Calcd for $C_{39}H_{36}O_4$: M, 568.2614.

3-Acetyl-2-methyl-4-(3,3-diphenyl-2-propenyl)-5,5-diphenyl-4,5-dihydrofuran (3f): Yellow liquid; IR 1663 (C=O); ^{1}H NMR δ=2.01 (3H, s, COMe), 2.08—2.17 (2H, m, -CH_2-), 2.25 (3H, s, Me), 4.03 (1H, br.t, J=6.0 Hz, >CH-), 5.70 (1H, t, J=8.0 Hz, =CH-), and 6.72—7.86 (20H, m, arom.H); MS m/z (rel intensity) 471 (100), 470 (M^+, 4), 458 (7), 337 (32), 227 (29), 183 (26), and 105 (7). Found: m/z 470.2236. Calcd for $C_{34}H_{30}O_2$: M, 470.2246.

Bis[4-acetyl-2,2-bis(4-chlorophenyl)-5-methyl-2,3-dihydro-3-furyl]methane (2g): Yellow liquid; IR 1660 (C=O); ^{1}H NMR δ=0.80—1.08 (2H, m, -CH_2-), 2.10 (6H, s, 2×COMe), 2.27 (7H, s, 2×Me), 4.0—4.3 (2H, m, >CH-), and 6.87—7.67 (16H, m, arom.H); MS m/z (rel intensity) 706 (M^+, 3), 704 (M^+, 2), 606 (5), 604 (4), 509 (3), 507 (2), 358 (64), 345 (31), 316 (7), 235 (12), 199 (9), and 139 (8). Found: m/z 704.1011. Calcd for $C_{39}H_{32}O_4{}^{35}Cl_4$: M, 704.1055.

3-Acetyl-4-[3,3-bis(4-chlorophenyl)-2-propenyl]-5,5-bis(4-chlorophenyl)-2-methyl-4,5-dihydrofuran (3g): Yellow liquid; IR 1697 (C=O); ^{1}H NMR δ=1.72—1.97 (2H, m, -CH_2-), 2.10 (3H, s, COMe), 2.22 (3H, s, Me), 3.70—4.18 (1H, m, >CH-), 5.5—5.8 (1H, m, =CH-), and 6.61—7.50 (16H, m, arom.H); MS m/z (rel intensity) 608, (M^+, 4), 606 (M^+, 3), 565 (35), 563 (26), 509 (18), 507 (15), 371 (13), 345 (60), 261 (17), 235 (36), and 139 (18). Found: m/z 608.0678; 606.0660. Calcd for $C_{34}H_{26}O_2{}^{35}Cl_3{}^{37}Cl$; $C_{34}H_{26}O_2{}^{35}Cl_4$: M, 608.0657; 606.0687.

Bis[4-acetyl-2,2-bis(4-methylphenyl)-5-methyl-2,3-dihydro-3-furyl]methane (2h): Yellow liquid; IR 1715 (C=O); ^{1}H NMR δ=0.75—1.40 (2H, m, -CH_2-), 2.17 (6H, s, 2×Me), 2.19 (6H, s, 2×Me), 2.23 (6H, s, 2×Me), 2.31 (6H, s, 2×Me), 3.65 (2H, br.t, J=7.0 Hz, 2×>CH-), and 6.77—7.47 (16H, m, arom.H); MS m/z (rel intensity) 624 (M^+, 65), 523 (5), 480 (3), 428 (4), 368 (3), 317 (65), 263 (17), 219 (28), 195 (40), 179 (25), and 105 (16). Found: m/z 624.3204. Calcd for $C_{43}H_{44}O_4$: M, 624.3240.

3-Acetyl-4-[3,3-bis(4-methylphenyl)-2-propenyl]-5,5-bis(4-methylphenyl)-2-methyl-4,5-dihydrofuran (3h); Yellow liquid; IR 1662 (C=O); ^{1}H NMR δ=1.99 (2H, m, -CH_2-), 2.27 (12H, s, 3×Me), 2.33 (6H, s, 2×Me), 3.93 (1H, br.t, J=6 Hz, >CH-), 5.55 (1H, t, J=7 Hz, =CH-), and 6.67—7.48 (16H, m, arom.H); MS m/z (rel intensity) 526 (M^+, 60), 482 (5), 426 (10), 346 (15), 304 (100), 284 (22), 262 (43), 221 (100), 195 (91), 179 (35), 119 (62), and 91 (32). Found: m/z 526.2902. Calcd for $C_{38}H_{38}O_2$: M, 526.2872.

1,2-Bis(4-acetyl-5-methyl-2,2-diphenyl-2,3-dihydro-3-furyl)ethane (2i): Yellow microcrystals (from benzene-petroleum ether), mp 220—222 °C; IR 1662 (C=O); ^{1}H NMR δ=0.78—1.01 (4H, m, 2×-CH_2-), 1.97 (6H, s, 2×COMe), 2.07 (6H, 2×Me), 3.30.—3.60 (2H, m, 2×>CH-), and 6.78—7.42 (20H, m, 4×Ph). Found: C, 82.31; H, 6.60%. Calcd for $C_{40}H_{38}O_4$: C, 82.44; H, 6.57%.

3-Acetyl-2-methyl-4-(4,4-diphenyl-3-butenyl)-5,5-diphenyl-4,5-dihydrofuran (3i): Colorless microcrystals (from benzene-petroleum ether), mp 109—110 °C; IR 1663 (C=O); ^{1}H NMR δ=1.35—1.78 (4H, m, 2×-CH_2-), 2.15 (3H, s, COMe), 2.19 (3H, s, Me), 3.68—3.95 (1H, m, >CH-), 5.57—5.88 (1H, m, =CH-), and 6.63—7.53 (20H, m, 4×Ph). Found: C, 86.55; H, 6.70%. Calcd for $C_{35}H_{32}O_2$: C, 86.74; H, 6.66%.

1,2-Bis[4-acetyl-2,2-bis(4-chlorophenyl)-5-methyl-2,3-dihydro-3-furyl]ethane (2j): Yellow microcrystals (from benzene-petroleum ether), mp 252—253 °C; IR 1665 (C=O); ^{1}H NMR δ=0.72—1.13 (4H, m, 2×-CH_2-), 2.15 (6H, s, 2×COMe), 2.18 (6H, s, 2×Me), 3.35—3.57 (2H, m, 2×>CH-), and 6.95—7.72 (16H, m, arom.H); MS m/z (rel intensity) 720 (M^+, 13), 718 (M^+, 10), 620 (23), 618 (17), 483 (8), 423 (4), 372 (60), 346 (32), 329 (18), 261 (15), 235 (26), 199 (20), and 125 (10). Found: m/z 720.1184; 718.1193. Calcd for $C_{40}H_{34}O_4{}^{35}Cl_3{}^{37}Cl$; $C_{40}H_{34}O_4{}^{35}Cl_4$: M, 720.1189; 718.1212.

3-Acetyl-4-[4,4-bis(4-chlorophenyl)-3-butenyl]-5,5-bis(4-chlorophenyl)-2-methyl-4,5-dihydrofuran (3j): Yellow microcrystals (from benzene-petroleum ether), mp 174—176 °C; IR 1665 (C=O); ^{1}H NMR δ=1.23—1.80 (4H, m, 2×-CH_2-), 2.23 (6H, s, COMe and Me), 3.67—3.97 (1H, m, >CH-), 5.73—6.07 (1H, m, =CH-), and 6.83—7.60 (16H, m, arom.H). Found: C, 67.58; H, 4.49%. Calcd for $C_{35}H_{28}O_2Cl_4$: C, 67.54; H, 4.53%.

1,2-Bis[4-acetyl-2,2-bis(4-methylphenyl)-5-methyl-2,3-dihydro-3-furyl]ethane (2k): Yellow liquid; IR 1665 (C=O); ^{1}H NMR δ=0.82—1.05 (4H, m, 2×-CH_2-), 1.96 (6H, s, 2×Me), 2.06 (6H, s, 2×Me), 2.22 (6H, s, 2×Me), 2.31 (6H, s, 2×Me), 3.25—3.57 (2H, m, 2×>CH-), and 6.77—7.35 (16H, m, arom.H); MS *m/z* (rel intensity) 638 (M^+, 50), 537 (27), 442 (15), 331 (90), 305 (66), 288 (37), 262 (46), 219 (63), 195 (100), 179 (81), 105 (80), and 91 (30). Found: *m/z* 638.3388. Calcd for $C_{44}H_{46}O_4$: M, 638.3396.

3-Acetyl-4-[4,4-bis(4-methylphenyl)-3-butenyl]-5,5-bis(4-methylphenyl)-2-methyl-4,5-dihydrofuran (3k): Yellow liquid; IR 1660 (C=O); ^{1}H NMR δ=1.12—1.85 (4H, m, 2×-CH_2-), 2.17 (3H, s, Me), 2.22 (3H, s, Me), 2.29 (9H, s, 3×Me), 2.38 (3H, s, Me), 3.68—3.98 (1H, m, >CH-), 5.58—5.88 (1H, m, =CH-), and 6.78—7.48 (16H, m, arom.H); MS *m/z* (rel intensity) 540 (M^+, 18), 306 (100), 263 (22), 234 (81), 219 (31), 195 (17), 105 (15). Found: *m/z* 540.3031. Calcd for $C_{39}H_{40}O_2$: M, 540.3028.

1,2-Bis[4-acetyl-2,2-bis(4-methoxyphenyl)-5-methyl-2,3-dihydro-3-furyl]ethane (2l): Yellow liquid; IR 1665 (C=O); ^{1}H NMR δ=0.71—1.18 (4H, m, 2×-CH_2-), 2.09 (6H,s, 2×Me), 2.13 (6H, s, 2×Me), 3.34—3.64 (2H, m, 2×>CH-), 3.76 (6H, s, 2×OMe), 3.83 (3H, s, OMe), 3.86 (3H, s, OMe), and 6.51—7.96 (16H, m, arom.H); MS *m/z* (rel intensity) 702 (M^+, 25), 602 (6), 475 (10), 364 (72), 338 (100), 227 (52), 211 (15), and 135 (23). Found: *m/z* 702.3201. Calcd for $C_{44}H_{46}O_8$: M, 702.3193.

4,4′-Dimethoxybenzophenone (6): Yellow needles (from ethanol), mp 140—141 °C (lit,[40] mp 144 °C)

Reaction of Terminal Dienes with [Co(acac)$_3$]. In order to determine the optimum reaction conditions for the formation of bis(dihydrofuran), the reactions were examined using diene (**1i**) changing molar ratio, solvent, and reaction temperature. The effect of additive was also tested. When **1i** was allowed to react with [Co(acac)$_3$] at the molar ratio of 1 : 6 in acetic acid at the reflux temperature, the best yield of **2i** was obtained. The reaction predominantly gave **2i** irrespective of the presence of an active methylene compound such as malonic acid, malonamide, and diethyl malonate. The results are shown in Table 4. Accordingly, the reaction with [Co(acac)$_3$] was conducted as follows. To a heated solution of a terminal diene (0.5—1.0 mmol) in acetic acid (30 cm^3), [Co(acac)$_3$] was added. The mixture was heated under reflux until its dark green solution turned pink. The solvent was evaporated in vacuo and the residue was triturated with 2M HCl (30 cm^3), followed by extraction with chloroform. The chloroform was removed in vacuo and the product residue was separated on TLC with chloroform as the developing solvent. The yields are summarized in Table 1.

Reaction of Terminal Dienes with Ethyl 3-Oxobutanoate in the Presence of [Mn(OAc)$_3$]. To a heated solution of a diene (0.5—1.0 mmol) and ethyl 3-oxobutanoate in acetic acid (30 cm^3), [Mn(OAc)$_3$] was added. The mixture was heated under reflux until its dark-brown color turned clear yellow. The solvent was removed and the residue was treated with the same work-up previously mentioned. The results are shown in Table 2.

3-Ethoxycarbonyl-2-methyl-4-(2,2-diphenylethenyl)-5,5-diphenyl-4,5-dihydrofuran (8a): Colorless microcrystals (from ethyl acetate-ehanol), mp 133—134 °C; IR 1686 (C=O); ^{1}H NMR δ=1.24 (3H, t, *J*=7.0 Hz, Me), 2.39 (3H, s, Me), 4.18 (2H, q, *J*=7.0 Hz, -CH_2-), 4.92 (1H, br.d, *J*=11.0 Hz, >CH-), 5.44 (1H, d, *J*=11.0 Hz, =CH-), and 6.54—7.91 (20H, m, 4×Ph). Found: C, 83.90; H, 6.16%. Calcd for $C_{34}H_{30}O_3$: C, 83.92; H, 6.21%.

1,2,4,4-Tetraphenyl-3-butene-1-one (10a):[41] Yellow liquid; IR 1679 (C=O); ^{1}H NMR δ=5.35 (1H, d, *J*=10.0 Hz, >CH-), 6.69 (1H, d, *J*=10.0 Hz, =CH-), and 6.89—7.85 (20H, m, arom.H); MS *m/z* (rel intensity) 374 (M^+, 1), 345 (13), 269 (100), 191 (43), 105 (45), and 91 (13).

4-[2,2-Bis(4-chlorophenyl)ethenyl]-5,5-bis(4-chlorophenyl)-3-ethoxycarbonyl-2-methyl-4,5-dihydrofuran (8b): Colorless prisms (from ethyl acetate-ethanol), mp 181—182 °C; IR 1686 (C=O); ^{1}H NMR δ=1.27 (3H, t, *J*=7.0 Hz, Me), 2.33 (3H, s, Me), 4.16 (2H, q, *J*=7.0 Hz, -CH_2-), 4.66 (1H, br.d, *J*=11.0 Hz, >CH-), 5.26 (1H, d, *J*=11.0 Hz, =CH-), and 6.36—7.78 (16H, m, arom.H). Found: C, 65.41; H, 4.25%. Calcd for $C_{34}H_{26}O_3Cl_4$: C, 65.40; H, 4.20%.

3-Ethoxycarbonyl-4-[2,2-bis(4-methylphenyl)ethenyl]-

Table 4. Reaction of 1,1,6,6-Tetraphenyl-1,5-hexadiene (**1i**) with [Co(acac)$_3$]

Entry	Solvent	Additive	Molar ratio[a]	Reaction time[b]	Recovered **1i**	Product (yield/%)[c]	
				h	%	**2i**	**3i**
1	Acetic acid	None	1 : 0 : 4	1.5		59	18
2		None	1 : 0 : 6	1.5		92	
3		None	1 : 0 : 8	1.5		88	
4[d]		None	1 : 0 : 6	16		68	
5	Propanoic acid	None	1 : 0 : 6	2.5	10	12	25
6	2,4-Pentanedione	None	1 : 0 : 6	24	85		
7	Benzene	None	1 : 0 : 6	24	93		
8	Acetic acid	$CH_2(CO_2H)_2$	1 : 6 : 8	0.7		79	
9		$CH_2(CONH_2)_2$	1 : 6 : 8	0.7		51	23
10		$CH_2(CO_2Et)_2$	1 : 6 : 8	1.0		46	
11		Ac_2O	1 : 10 : 6	2.0		80	15

a) **1i**: Additive: [Co(acac)$_3$]. b) The reaction time shows consumption time of the oxidant. c) The yield based on **1i** added. d) The reaction was carried out at 100 °C.

5,5-bis(4-methylphenyl)-2-methyl-4,5-dihydrofuran (8c): Colorless needles (from ethanol), mp 133—135 °C; IR 1687 (C=O); ^{1}H NMR δ=1.23 (3H, t, J=7.0 Hz, Me), 2.19 (6H, s, 2×Me), 2.29 (6H, s, 2×Me), 2.42 (3H, s, Me), 4.11 (2H, q, J=7.0 Hz, -CH_2-), 4.71 (1H, br. d, J=11.0 Hz, >CH-), 5.21 (1H, d, J=11.0 Hz, =CH-), and 6.29—7.52 (16H, m, arom.H). Found: C, 84.05; H, 7.01%. Calcd for $C_{38}H_{38}O_3$: C, 84.10; H, 7.06%.

1,2,4,4-Tetrakis(4-methylphenyl)-3-butene-1-one (10c): Colorless needles (from ethyl acetate-ethanol), mp 130—131 °C; IR 1675 (C=O); ^{1}H NMR δ=2.27 (6H, s, 2×Me), 2.31 (3H, s, Me), 2.39 (3H, s, Me), 5.36 (1H, d, J=10.0 Hz, >CH-), 6.58 (1H, d, J=10.0 Hz, =CH-), and 6.87—7.80 (16H, m, arom.H); MS m/z (rel intensity) 430 (M^+, 1), 311 (100), 219 (33), 203 (3), 119 (6), and 91 (4). Found: C, 89.34; H, 7.03%. Calcd for $C_{32}H_{30}O$: C, 89.26; H, 7.02%.

3-Ethoxycarbonyl-2-methyl-5-[(*E*)-2-phenylethenyl]-4-phenyl-4,5-dihydrofuran (9d): Yellow liquid; IR 1693 (C=O); ^{1}H NMR δ=0.95 (3H, t, J=7.0 Hz, Me), 2.33 (3H, d, J=2.0 Hz, Me), 3.91 (2H, q, J=7.0 Hz, -CH_2-), 4.12 (1H, q, J=2.0 Hz, >CH-), 4.90 (1H, t, J=6.0 Hz, >CH-O-), 6.15 (1H, dd, J=6.0 and 16.0 Hz, =CH-), 6.48 (1H, d, J=16.0 Hz, =CH-), and 6.88—7.45 (10H, m, 2×Ph); MS m/z (rel intensity) 334 (M^+, 84), 305 (3), 292 (66), 279 (17), 260 (14), 245 (100), 231 (28), 217 (78), 202 (28), 180 (30), 167 (18), 149 (30), 115 (25), and 105 (50). Found: m/z 334.1541. Calcd for $C_{22}H_{22}O_3$: M, 334.1569.

3-Ethoxycarbonyl-2,4,4-trimethyl-5-(2-methyl-1-propenyl)-4,5-dihydrofuran (9e): Colorless liquid; IR 1678 (C=O); ^{1}H NMR δ=1.00 (3H, s, Me), 1.19 (3H, s, Me), 1.26 (3H, t, J=7.0 Hz, Me), 1.72 (3H, d, J=1.7 Hz, Me), 1.81 (3H, d, J=1.7 Hz, Me), 2.09 (3H, s, Me), 4.11 (2H, q, J=7.0 Hz, -CH_2-), 4.66 (1H, d, J=10.0 Hz, >CH-), and 5.27 (1H, br.d, J=10.0 Hz, =CH-); MS m/z (rel intensity) 238 (M^+, 59), 223 (100), 195 (67), 149 (73), 121 (88), and 107 (26). Found: m/z 238.1576. Cacld for $C_{14}H_{22}O_3$: M, 238.1569.

Bis(4-ethoxycarbonyl-5-methyl-2,2-diphenyl-2,3-dihydro-3-furyl)methane (7f): Yellow liquid; IR 1685 (C=O); ^{1}H NMR δ=0.71—1.09 (2H, m, -CH_2-), 1.24 (6H, t, J=7.0 Hz, 2×Me), 2.12 (6H, s, 2×Me), 3.38—3.88 (2H, m, 2× >CH-), 4.15 (4H, q, J=7.0 Hz, 2×-CH_2-), and 6.68—7.84 (20H, m, 4×Ph); MS m/z (rel intensity) 628 (M^+, 1), 583 (3), 320 (100), 278 (24), 191 (27), and 105 (21). Found: m/z 628.2833. Calcd for $C_{41}H_{40}O_6$: M, 628.2825.

Bis[2,2-bis(4-chlorophenyl)-4-ethoxycarbonyl-5-methyl-2,3-dihydro-3-furyl]methane (7g): Yellow liquid; IR 1681 (C=O); ^{1}H NMR δ=0.69—1.12 (2H, m, -CH_2-), 1.26 (6H, t, J=7.0 Hz, 2×Me), 2.15 (6H, s, 2×Me), 3.19—3.66 (2H, m, 2×>CH-), 4.18 (4H, q, J= 7.0 Hz, 2×-CH_2-), and 6.76—7.69 (16H, m, arom.H); MS m/z (rel intensity) 766 (M^+, 2), 764 (M^+, 1), 634 (3), 632 (2), 388 (100), 346 (16), 302 (12), 259 (10), 199 (12), 167 (22), 149 (50), and 113 (7). Found: m/z 766.1257; 764.1323. Calcd for $C_{41}H_{36}O_6{}^{35}Cl_3{}^{37}Cl$; $C_{41}H_{36}O_6{}^{35}Cl_4$: M, 766.1244; 764.1266.

Bis[4-ethoxycarbonyl-2,2-bis(4-methylphenyl)-5-methyl-2,3-dihydro-3-furyl]methane (7h): Yellow liquid; IR 1687 (C=O); ^{1}H NMR δ=0.73—1.46 (2H, m, -CH_2-), 1.23 (6H, t, J=7.0 Hz, 2×Me), 2.19 (6H, s, 2×Me), 2.29 (6H, s, 2×Me), 2.42 (6H, s, 2×Me), 3.61—3.70 (2H, m, 2×>CH-), 4.11 (4H, q, J=7.0 Hz, 2×-CH_2-), and 6.60—7.53 (16H, m, arom.H); MS m/z (rel intensity) 684 (M^+, 1), 639 (3), 348 (100), 306 (27), 261 (10), and 195 (5). Found: m/z 684.3441. Calcd for $C_{45}H_{48}O_6$: M, 684.3451.

1,2-Bis(4-ethoxycarbonyl-5-methyl-2,2-diphenyl-2,3-dihydro-3-furyl)ethane (7i): Colorless microcrystals (from ethyl acetate/ethanol), mp 162—164 °C; IR 1690 (C=O); ^{1}H NMR δ=0.84—1.11 (4H, m, 2×-CH_2-), 1.20 (6H, t, J=7.0 Hz, 2×Me), 2.09 (6H, s, 2×Me), 3.33—3.71 (2H, m, 2× >CH-), 4.09 (4H, q, J=7.0 Hz, 2×-CH_2-), and 6.98—7.61 (20H, m, 4×Ph); MS m/z (rel intensity) 642 (M^+, 5), 596 (8), 550 (5), 512 (47), 466 (8), 429 (7), 383 (8), 334 (37), 307 (16), 245 (17), 193 (17), 149 (13), and 105 (30). Found: C, 78.37; H, 6.53%; m/z 642.2990. Calcd for $C_{42}H_{42}O_6$: C, 78.48; H, 6.59%; M, 642.2982.

1,2-Bis[2,2-bis(4-chlorophenyl)-4-ethoxycarbonyl-5-methyl-2,3-dihydro-3-furyl]ethane (7j): Colorless microcrystals (from benzene-petroleum ether), mp 103—105 °C; IR 1686 (C=O); ^{1}H NMR δ=0.82—1.09 (4H, m, 2×-CH_2-), 1.12 (6H, t, J=7.0 Hz, 2×Me), 2.11 (6H, s, 2×Me), 3.19—3.49 (2H, m, 2×>CH-), 4.07 (4H, q, J=7.0 Hz, 2×-CH_2-), and 6.89—7.42 (16H, m, arom.H); MS m/z (rel intensity) 780 (M^+, 4), 778 (M^+, 3), 734 (15), 732 (10), 688 (6), 686 (4), 650 (50), 648 (40), 604 (7), 602 (4), 543 (2), 497 (12), 451 (10), 402 (100), 375 (24), 356 (20), 261 (22), 235 (18), 199 (26), 165 (6), and 139 (15). Found: m/z 780.1308; 778.1379. Calcd for $C_{42}H_{38}O_6{}^{35}Cl_3{}^{37}Cl$; $C_{42}H_{38}O_6{}^{35}Cl_4$: M, 780.1401; 778.1423.

1,2-Bis[4-ethoxycarbonyl-2,2-bis(4-methylphenyl)-5-methyl-2,3-dihydro-3-furyl]ethane (7k): Colorless needles (from ethyl acetate-ethanol), mp 161—163 °C; IR 1683 (C=O); ^{1}H NMR δ=0.70—1.06 (4H, m, 2×-CH_2-), 1.23 (6H, t, J=7.0 Hz, 2×Me), 2.07 (6H, s, 2×Me), 2.28 (6H, s, 2×Me), 2.34 (6H, s, 2×Me), 3.19—3.49 (2H, m, 2×>CH-), 4.02 (4H, q, J=7.0 Hz, 2×-CH_2-), and 6.81—7.33 (16H, m, arom.H). Found: C, 79.06; H, 7.18%. Calcd for $C_{46}H_{50}O_6$: C, 79.05; H, 7.21%.

1,2-Bis[4-ethoxycarbonyl-2,2-bis(4-methoxyphenyl)-5-methyl-2,3-dihydro-3-furyl]ethane (7l): Colorless microcrystals (from benzene-petroleum ether), mp 97—98 °C; IR 1686 (C=O); ^{1}H NMR δ=0.85—1.08 (4H, m, 2×-CH_2-), 1.23 (6H, t, J=7.0 Hz, 2×Me), 2.08 (6H, s, 2×Me), 3.18—3.48 (2H, m, 2×>CH-), 3.74 (6H, s, 2×OMe), 3.81 (6H, s, 2×OMe), 4.07 (4H, q, J=7.0 Hz, 2×-CH_2-), and 6.58—7.38 (16H, m, arom.H); MS m/z (rel intensity) 762 (M^+, 24), 716 (6), 674 (9), 652 (18), 632 (70), 606 (18), 586 (13), 562 (7), 535 (15), 498 (24), 443 (5), 394 (100), 348 (47), 293 (38), 253 (35), 227 (66), 211 (22), 165 (7), and 135 (24). Found: m/z 762.3378. Calcd for $C_{46}H_{50}O_{10}$: M, 762.3404.

Reaction of Terminal Dienes with Ethyl 3-Oxobutanoate in the Presence of [Co(OAc)$_3$]. A mixture of a diene (0.5 mmol) and ethyl 3-oxobutanoate (3 mmol) was heated under reflux in acetic acid (30 cm^3) and then [Co(OAc)$_3$] (4 mmol) was added. The mixture was continued to be heated under reflux until a dark green color turned pink. On cooling, the solvent was removed in vacuo and the residue was treated by the procedure previously described. The products and their yields are shown in Table 3.

3-Ethoxycarbonyl-2-methyl-4-(4,4-diphenyl-3-butenyl)-5,5-diphenyl-4,5-dihydrofuran (8i): Colorless needles (from ethyl acetate-ethanol), mp 113—114 °C; IR 1683 (C=O); ^{1}H NMR δ=1.20 (3H, t, J=7.0 Hz, Me), 1.39—1.99 (4H, m, 2×-CH_2-), 2.20 (3H, s, Me), 3.77 (1H, br.t, J=5.0 Hz, >CH-), 4.07 (2H, q, J=7.0 Hz, -CH_2-), 5.73 (1H t, J=7.0 Hz, =CH-), and 6.82—7.52 (20H, m, 4×Ph). Found: C, 84.17; H, 6.66%. Calcd for $C_{36}H_{34}O_3$: C, 84.01; H, 6.66%.

4-[4,4-Bis(4-chlorophenyl)-3-butenyl]-5,5-bis(4-chlorophenyl)-3-ethoxycarbonyl-2-methyl-4,5-dihydrofuran (8j):

Yellow liquid; IR 1684 (C=O); ^{1}H NMR δ=1.24 (3H, t, J=7.0 Hz, Me), 1.47—1.91 (4H, m, 2×-CH_2-), 2.20 (3H, s, Me), 3.70 (1H, br.t, J=5.0 Hz, >CH-), 4.14 (2H, q, J=7.0 Hz, -CH_2-), 5.77 (1H, t, J=7.0 Hz, =CH-), and 6.81—7.84 (16H, m, arom.H); MS m/z (rel intensity) 652 (M^+, 8), 650 (M^+, 6), 561 (3), 559 (2), 522 (3), 520 (2), 389 (10), 343 (27), 301 (8), 274 (100), 239 (77), 199 (26), 165 (16), and 125 (22). Found: m/z 652.0901; 650.0922. Calcd for $C_{36}H_{30}O_3{}^{35}Cl_3{}^{37}Cl$; $C_{36}H_{30}O_3{}^{35}Cl_4$: M, 652.0926; 650.0949.

3-Ethoxycarbonyl-4-[4,4-bis(4-methylphenyl)-3-butenyl]-5,5-bis(4-methylphenyl)-2-methyl-4,5-dihydrofuran (8k): Yellow liquid; IR 1685 (C=O); ^{1}H NMR δ=1.22 (3H, t, J=7.0 Hz, Me), 1.44—1.87 (4H, m, 2×-CH_2-), 2.22 (3H, s, Me), 2.26 (3H, s, Me), 2.29 (6H, s, 2×Me), 2.37 (3H, s, Me), 3.77 (1H, br.t, J=6.0 Hz, >CH-), 4.12 (2H, q, J=7.0 Hz, -CH_2-), 5.72 (1H, t, J=7.0 Hz, =CH-), and 6.77—7.47 (16H, m, arom. H); MS m/z (rel intensity) 570 (M^+, 10), 525 (4), 440 (3), 391 (3), 349 (10), 335 (5), 303 (20), 290 (15), 275 (7), 261 (10), 234 (100), 219 (45), 195 (14), 143 (6), 129 (12), and 105 (18). Found: m/z 570.3125. Calcd for $C_{40}H_{42}O_3$: M, 570.3134.

Reactions of Terminal Dienes (1i—l) with Ethyl Hydrogen Malonate in the Presence of [Mn(OAc)$_3$]. A mixture of a diene (0.5—1.0 mmol) and ethyl hydrogen malonate was heated under reflux in acetic acid (30 cm^3) and then [Mn(OAc)$_3$] was added. The mixture was continued to be heated under reflux until a dark-brown color turned clear yellow. After removal of the solvent, the residue was triturated with 2M HCl (30 cm^3). The aqueous solution was extracted with chloroform and separated on TLC. The product and its yield are shown in Table 3.

2-Ethoxycarbonyl-3-(4,4-diphenyl-3-butenyl)-4,4-diphenyl-2-buten-4-olide (11i): Colorless microcrystals (from methanol), mp 181—183 °C; IR 1785 and 1730 (C=O); ^{1}H NMR δ=0.47 (3H, t, J=7.0 Hz, Me), 1.09—1.92 (2H, m, -CH_2-), 2.26—2.96 (2H, m, -CH_2-), 4.28 (2H, q, J=7.0 Hz -CH_2-), and 6.89—7.69 (21H, m, =CH- and 4×Ph); MS m/z (rel intensity) 514 (M^+, 65), 496 (28), 470 (57), 450 (20), 424 (40), 397 (46), 303 (29), 275 (50), 259 (30), 229 (35), 215 (42), 193 (100), 167 (60), 115 (30), and 105 (62). Found: C, 81.48; H, 5.88%. Calcd for $C_{35}H_{30}O_4$: C, 81.69; H, 5.88%.

The reaction of **1i** with ethyl hydrogen malonate in the presence of [Mn(OAc)$_3$] at the molar ratio of 1:6:7 under the similar reaction conditions was completed for 10 min to give a complex mixture, from which **11i** (46%) was obtained as an only isolable product.

3-[4,4-Bis(4-chlorophenyl)-3-butenyl]-4,4-bis(4-chlorophenyl)-2-ethoxycarbonyl-2-buten-4-olide (11j): Colorless needles (from ethyl acetate-ethanol), mp 195—197 °C; IR 1775 and 1730 (C=O); ^{1}H NMR δ=0.57 (3H, t, J=7.0 Hz, Me), 1.09—3.15 (4H, m, 2×-CH_2-), 4.18 (2H, q, J=7.0 Hz, -CH_2-), and 6.88—7.85 (17H, m, =CH- and arom.H); MS m/z (rel intensity) 652 (M^+, 45), 650 (M^+, 33), 634 (37), 632 (27), 606 (59), 604 (31), 588 (19), 586 (14), 535 (26), 533 (22), 490 (8), 437 (9), 389 (35), 372 (20), 343 (75), 261 (100), 235 (37), 202 (15), 165 (20), and 139 (55). Found: m/z 652.0586; 650.0585. Calcd for $C_{35}H_{26}O_4{}^{35}Cl_3{}^{37}Cl$; $C_{35}H_{26}O_4{}^{35}Cl_4$: M, 652.0556; 650.0585.

2-Ethoxycarbonyl-3-[4,4-bis(4-methylphenyl)-3-butenyl]-4,4-bis(4-methylphenyl)-2-buten-4-olide (11k): Colorless needles (from methanol), mp 155—157 °C; IR 1781 and 1729 (C=O); ^{1}H NMR δ=0.50 (3H, t, J=7.0 Hz, Me), 0.72—3.13 (4H, m, 2×-CH_2-), 2.19 (6H, s, 2×Me), 2.26 (6H, s, 2×Me), 4.15 (2H, q, J=7.0 Hz, -CH_2-), and 6.77—7.85 (17H, m, =CH- and arom.H); MS m/z (rel intensity) 570 (M^+, 38), 552 (17), 526 (54), 506 (13), 480 (40), 453 (53), 375 (11), 349 (22), 332 (15), 305 (39), 287 (12), 257 (16), 243 (21), 221 (100), 195 (38), 165 (13), and 119 (33). Found: m/z 570.2776. Calcd for $C_{39}H_{38}O_4$: M, 570.2770.

2-Ethoxycarbonyl-3-[4,4-bis(4-methoxyphenyl)-3-butenyl]-4,4-bis(4-methoxyphenyl)2-buten-4-olide (11l): Colorless needles (from benzene-petroleum ether), mp 143—144 °C; IR 1780 and 1729 (C=O); ^{1}H NMR δ=0.55 (3H t, J=7.0 Hz, Me), 1.40—1.83 (2H, m, -CH_2-), 2.27—2.97 (2H, m, -CH_2-), 3.67 (6H, s, 2×OMe), 3.72 (6H, s, 2×OMe), 4.17 (2H, q, J=7.0 Hz, -CH_2-), and 6.51—7.57 (17H, m, =CH- and arom.H). Found: C, 73.54; H, 6.00%. Calcd for $C_{39}H_{38}O_8$: C, 73.80; H, 6.04%.

Cross-Over Experiment for the Formation of Rearrangement Product. The butadienes **1a** (185.4 mg; 0.5 mmol) and **1c** (203.2 mg; 0.5 mmol) were dissolved in acetic acid (30 cm^3) upon heating and then [Mn(OAc)$_3$] (742.6 mg; 1 mmol=3 equivalents) was added. The mixture was heated under reflux until the dark Mn(III) ion completely disappeared (15 min). The solvent was removed in vacuo and the residue was worked up by the same procedure previously mentioned. After TLC separation, the oxidative rearrangement products **10a** (61.5 mg; 33%) and **10c** (173.4 mg; 81%) were obtained and **1a** (85.7 mg; 46%) was recovered. No cross-over compound was isolated.

We are grateful for the financial support of this work by a Grant-in-Aid for Encouragement of Young Scientists No. 62740301 from the Ministry of Education, Science and Culture. The authors wish to thank Dr. Terry Marriott of the Department of Chemistry, Rice University, Houston, Texas, U.S.A., for his measurement of high-resolution mass spectra. We also acknowledge Mr. Yasunori Sudoh of the Taiho Pharmaceutical Co., Inc., Tokushima, for his arrangement of the measurements of high-resolution mass spectra.

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