Reaction of Oligomethylene Di(3-oxobutanoate) with 1,1-Disubstituted Alkenes and Molecular Oxygen in the Presence of Manganese(II and/or III) Acetate

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Received May 8, 1995

The reactions of 1,1-disubstituted ethenes with oligomethylene di(3-oxobutanoate) in the presence of manganese(II and/or III) acetate and atmospheric oxygen yielded an ω-(3-oxobutanoyloxy)alkyl 6,6-diaryl-3-hydroxy-3-methyl-1,2-dioxane-4-carboxylate, oligomethylene di(6,6-diaryl-3-hydroxy-3-methyl-1,2-dioxane-4-carboxylate)s, ω-hydroxyalkyl 6,6-diaryl-3-hydroxy-3-methyl-1,2-dioxane-4-carboxylates, an ω-(3-oxobutanoyloxy)alkyl 5,5-diaryl-2-methyl-4,5-dihydrofuran-3-carboxylate, oligomethylene di(5,5-diaryl-2-methyl-4,5-dihydrofuran-3-carboxylate)s, ω-hydroxyalkyl 5,5-diaryl-2-methyl-4,5-dihydrofuran-3-carboxylates, and an oligomethylene diester bearing a substituted 1,2-dioxane ring and a substituted 4,5-dihydrofuran ring. The reaction of the 1,2-dioxan-3-ols with acid gave the corresponding compounds bearing furan rings. The reaction of 1,1,6,6-tetraaryl-1,5-hexadienes with oligomethylene di(3-oxobutanoate) in the presence of manganese(III) acetate yielded macrocyclic diesters bearing two 4,5-dihydrofuran rings.

J. Heterocyclic Chem., **32**, 1783 (1995).

Introduction.

We recently reported that the manganous acetate (manganese(II) acetate) or manganic acetate (manganese(III) acetate)-mediated free-radical cyclization of alkenes with 1,3-diones [1-3], acetoacetamides [1,4] or β-keto esters [5] and atmospheric oxygen gave 1,2-dioxan-3-ols in good yields. It was found that treatment of alkenes with acetoacetamides and oxygen in the presence of manganese(III) acetate gave the corresponding 1,2-dioxan-3-ols most effectively. Manganese(II) acetate, on the other hand, gave better yields for the formation of 1,2-dioxan-3-ols in the reaction of alkenes with 1,3-diketones bearing active methine and oxygen. It was also reported that a combination of manganese(II) acetate and a catalytic amount of manganese(III) acetate afforded the 1,2-dioxan-3-ols in good yields in the reaction of alkene with β-keto esters and oxygen by minimizing the formation of by-products [5]. We have further investigated the synthesis of 1,2-dioxane derivatives by the reaction of alkenes with oligomethylene di(3-oxobutanoate) and oxygen in the presence of various transition metal salts with particular attention to the preparation of compounds bearing two 1,2-dioxane rings, since some of the naturally occurring 1,2-dioxan-3-ols inhibit root formation [6]. The syntheses of compounds bearing two of 1,2-dioxane, 4,5-dihydrofuran, or furan rings are also described in this paper.

Results and Discussion.

Reaction of 1,1-Diphenylethene (**1a**) with Ethylene Di(3-oxobutanoate) (**2_2**) and Oxygen in the Presence of Various Metal Salts at Room Temperature.

When the reaction of 1,1-diphenylethene (**1a**) with ethylene di(3-oxobutanoate) (**2_2**) and oxygen in the presence of a mixture of manganese(II) and manganese(III) acetates was carried out at room temperature, the products were 2-(3-oxobutanoyloxy)ethyl 3-hydroxy-3-methyl-6,6-diphenyl-1,2-dioxane-4-carboxylate (**$3a_2$**), ethylene di(3-hydroxy-3-methyl-6,6-diphenyl-1,2-dioxane-4-carboxylate) (**$4a_2$**), 2-hydroxyethyl 3-hydroxy-3-methyl-6,6-diphenyl-1,2-dioxane-4-carboxylate (**$5a_2$**), and ethylene (3-hydroxy-3-methyl-6,6-diphenyl-1,2-dioxane-4-carboxylate) (2-methyl-5,5-diphenyl-4,5-dihydrofuran-3-carboxylate) (**$6a_2$**) (Scheme 1). Benzophenone and 2-hydroxy-2,2-diphenylethyl acetate were also formed as the by-products. The structures of the products were determined by means of ^{1}H nmr, ^{13}C nmr, ir spectroscopies, and elemental analyses, as well as by comparison of the spectra with those of methyl 6,6-diaryl-3-hydroxy-3-methyl-1,2-dioxane-4-carboxylate [5]. Yields of the products varied depending on the molar ratio of **1a**:**2_2**: manganese(II):manganese(III). The maximum yield for **$3a_2$** was attained when the molar ratio was 1:3:1:0.2 in which **2_2** was used in a large excess (Table 1, entry 1). With decreasing the molar ratio of **2_2** the yield of product **$4a_2$** increased (entries 2-4). When the reaction of **1a** with **2_2** was carried out in the presence of manganese(III) acetate and oxygen at room temperature, compound **$4a_2$** was still the major product in slightly decreased yield, but compound **$6a_2$** was also formed in considerable amount (entry 5).

The ^{13}C nmr spectrum of $\mathbf{4a_2}$ in deuteriochloroform showed a methyl carbon signal at $\delta = 24.3$, a methylene carbon at $\delta = 31.3$, a methine carbon at $\delta = 45.7$, methylene carbons bearing an oxygen atom at $\delta = 62.5$, a carbon attached to two phenyl groups at $\delta = 85.2$, a carbon attached to two oxygen atoms at $\delta = 98.6$, aromatic carbons at $\delta = 125.7$, 126.7, 127.4, 128.1, 128.4, 128.5, 140.7 and 143.2, and carbonyl carbons at $\delta = 170.7$ and 170.8. The two peaks for the carbonyl carbon would indicate that the compound consisted of two diastereomers.

The reactions were examined for 1,1-bis(4-chlorophenyl)ethene (**1b**) and 1,1-bis(4-methylphenyl)ethene (**1c**), ethylene di(3-oxobutanoate) ($\mathbf{2_2}$), trimethylene di(3-oxobutanoate) ($\mathbf{2_3}$), and tetramethylene di(3-oxobutanoate) ($\mathbf{2_4}$) using manganese(III) acetate, and a combination of manganese(II) and manganese(III) acetates. The results are summarized in Table 1 (entries 6-13). The reactions using a combination of manganese(II) and manganese(III) acetates always gave **4** in better yields than those in the reactions with manganese(III) acetate alone.

Compound $\mathbf{5a_2}$ could formally be obtained by the hydrolysis of $\mathbf{3a_2}$ or $\mathbf{4a_2}$. In fact, treatments of $\mathbf{3a_2}$ and $\mathbf{4a_2}$ with acetic acid containing manganese(II) acetate tetrahydrate at room temperature for 24 hours yielded $\mathbf{5a_2}$ in 19% and 6% yields, respectively.

Reactions of 1,1-Diarylethene **1a-c** with Oligomethylene Di(3-oxobutanoate) $\mathbf{2_n}$ in the Presence of Manganese(III) Acetate at Elevated Temperature.

When the reaction of **1a** with $\mathbf{2_2}$ was carried out in the presence of manganese(III) acetate under argon atmosphere at 100°, major products were 2-(3-oxobutanoyloxy)ethyl 2-methyl-5,5-diphenyl-4,5-dihydrofuran-3-carboxylate ($\mathbf{7a_2}$), ethylene di(2-methyl-5,5-diphenyl-4,5-dihydrofuran-3-carboxylate) ($\mathbf{8a_2}$), and 2-hydroxyethyl 2-methyl-5,5-diphenyl-4,5-dihydrofuran-3-carboxylate ($\mathbf{9a_2}$) (Table

Table 1

Reactions of 1,1-Diarylethenes **1a-c** with Oligomethylene Di(3-oxobutanoate)s $\mathbf{2_n}$ in the Presence of Manganese Acetates in Acetic Acid at 23°C

Entry	Substrate		Molar ratio [a]	Time hours	Product composition (yield/%) [b]					
1	**1a**	$\mathbf{2_2}$	1:3:1:0.2	2.5	$\mathbf{3a_2}$ (60)	$\mathbf{4a_2}$ (11)	$\mathbf{5a_2}$ (11)			[c]
2	**1a**	$\mathbf{2_2}$	1:2:1:0.2	5	$\mathbf{3a_2}$ (32)	$\mathbf{4a_2}$ (23)	$\mathbf{5a_2}$ (17)			[d]
3	**1a**	$\mathbf{2_2}$	1:1:1:0.2	20	$\mathbf{3a_2}$ (2)	$\mathbf{4a_2}$ (52)	$\mathbf{5a_2}$ (4)	$\mathbf{6a_2}$ (5)		
4	**1a**	$\mathbf{2_2}$	1:0.5:1:0.2	20		$\mathbf{4a_2}$ (48)	$\mathbf{5a_2}$ (22)			[d,e]
5	**1a**	$\mathbf{2_2}$	1:1:0:1	24		$\mathbf{4a_2}$ (38)		$\mathbf{6a_2}$ (20)		
6	**1b**	$\mathbf{2_2}$	1:1:1:0.2	20		$\mathbf{4b_2}$ (36)	$\mathbf{5b_2}$ (16)			[f,g]
7	**1b**	$\mathbf{2_2}$	1:1.5:0:1	20		$\mathbf{4b_2}$ (14)	$\mathbf{5b_2}$ (10)			[g]
8	**1c**	$\mathbf{2_2}$	1:1:1:0.2	20		$\mathbf{4c_2}$ (48)	$\mathbf{5c_2}$ (33)	$\mathbf{6c_2}$ (7)		
9	**1c**	$\mathbf{2_2}$	1:1.5:0:1	24		$\mathbf{4c_2}$ (20)	$\mathbf{5c_2}$ (14)	$\mathbf{6c_2}$ (6)		
10	**1a**	$\mathbf{2_3}$	1:1:1:0.2	20		$\mathbf{4a_3}$ (30)	$\mathbf{5a_3}$ (20)	$\mathbf{6a_3}$ (5)		[d]
11	**1a**	$\mathbf{2_3}$	1:1.5:0:1	20		$\mathbf{4a_3}$ (15)	$\mathbf{5a_3}$ (11)		$\mathbf{9a_3}$ (4)	
12	**1a**	$\mathbf{2_4}$	1:1:1:0.2	20		$\mathbf{4a_4}$ (30)	$\mathbf{5a_4}$ (20)			[d]
13	**1a**	$\mathbf{2_4}$	1:1.5:0:1	24		$\mathbf{4a_4}$ (23)	$\mathbf{5a_4}$ (2)	$\mathbf{6a_4}$ (4)	$\mathbf{9a_4}$ (1)	

[a] Alkene:ester:manganese(II) acetate:manganese(III) acetate. [b] All the yields are given for the chromatographically purified materials based on the alkene used. [c] Compound $\mathbf{2_2}$ (10%) was recovered. [d] Benzophenone was obtained in 0.3-7% yields. [e] Compound **1a** (22%) was recovered. [f] 4,4'-Dichlorobenzophenone (3%) was obtained. [g] 2,2-Bis(4-chlorophenyl)-2-hydroxyethyl acetate was obtained in 4-6% yields.

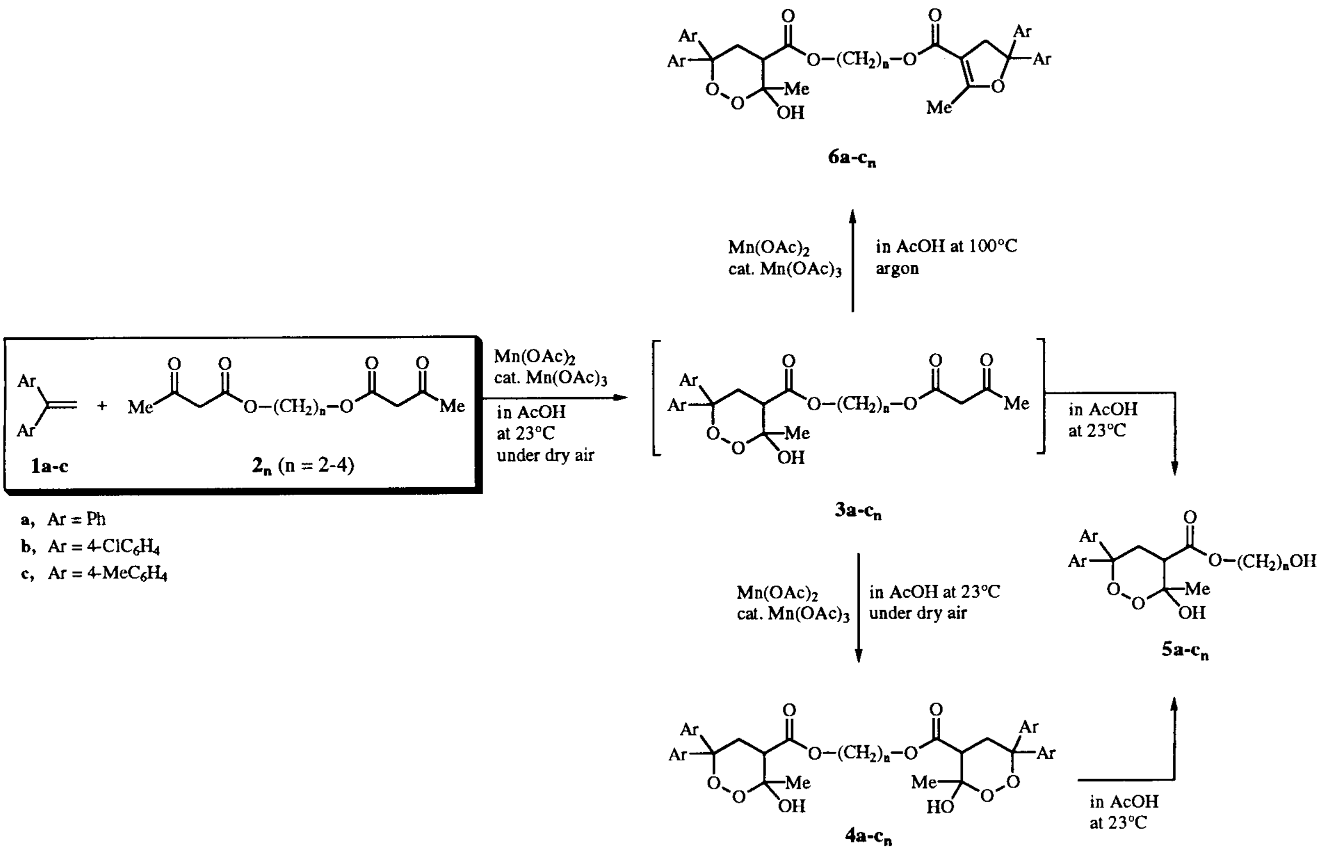
Table 2

Reactions of 1,1-Diarylethenes **1a-c** with Oligomethylene Di(3-oxobutanoate) $\mathbf{2_n}$ in the Presence of Manganese(III) Acetate in Acetic Acid at 100°C

Entry	Substrate		Molar ratio [a]	Time minutes	Recovery/%	Product composition (yield/%) [b]			
14	**1a**	$\mathbf{2_2}$	1:2:2.5	3	$\mathbf{2_2}$ (13)	$\mathbf{7a_2}$ (45)	$\mathbf{8a_2}$ (12)		
15	**1a**	$\mathbf{2_2}$	1:2:2.0	3	$\mathbf{2_2}$ (15)	$\mathbf{7a_2}$ (38)	$\mathbf{8a_2}$ (7)		
16	**1a**	$\mathbf{2_2}$	1:2:1.5	3	$\mathbf{2_2}$ (24)	$\mathbf{7a_2}$ (30)	$\mathbf{8a_2}$ (5)		
17	**1a**	$\mathbf{2_2}$	1:0.5:3.5	30			$\mathbf{8a_2}$ (70)	$\mathbf{9a_2}$ (25)	
18	**1a**	$\mathbf{2_2}$	1:0.5:2.5	3	**1a** (12)	$\mathbf{7a_2}$ (12)	$\mathbf{8a_2}$ (45)	$\mathbf{9a_2}$ (23)	[c]
19	**1a**	$\mathbf{2_2}$	1:0.5:1.5	3	**1a** (32)	$\mathbf{7a_2}$ (41)	$\mathbf{8a_2}$ (12)	$\mathbf{9a_2}$ (14)	
20	**1b**	$\mathbf{2_2}$	1:0.5:3.5	30			$\mathbf{8b_2}$ (45)	$\mathbf{9b_2}$ (21)	
21	**1c**	$\mathbf{2_2}$	1:0.5:3.5	30			$\mathbf{8c_2}$ (80)	$\mathbf{9c_2}$ (16)	
22	**1a**	$\mathbf{2_3}$	1:0.5:3.5	30			$\mathbf{8a_3}$ (62)	$\mathbf{9a_3}$ (25)	
23	**1a**	$\mathbf{2_4}$	1:0.5:3.5	30			$\mathbf{8a_4}$ (61)	$\mathbf{9a_4}$ (21)	

[a] Alkene:ester:manganese(III) acetate. [b] All the yields are given for the chromatographically purified materials based on the alkene used. [c] Benzophenone (4%) was obtained.

Scheme 1



2) (Scheme 2). The yields also varied depending on the molar ratio of **1a**:**2$_2$**:manganese(III) acetate. In a reaction of **1a** with **2$_2$** at higher molar ratio **7a$_2$** was the predominant product (entries 14-16). The yield for **8a$_2$**, on the other hand, was optimized in the reaction at a molar ratio of 1:0.5:3.5 for **1a**:**2$_2$**:manganese(III) acetate up to a 70% yield (entry 17). Then the reactions were examined for 1,1-bis(4-chlorophenyl)ethene (**1b**), 1,1-bis(4-methylphenyl)ethene (**1c**), ethylene di(3-oxobutanoate) (**2$_2$**), trimethylene di(3-oxobutanoate) (**2$_3$**), and tetramethylene di(3-oxobutanoate) (**2$_4$**) using manganese(III) acetate, and the yields are listed in Table 2 (entries 20-23). Oligomethylene di(5,5-diaryl-2-methyl-4,5-dihydrofuran-3-carboxylate)s **8a$_n$-8c$_n$** were formed in moderate to good yields together with ω-hydroxyalkyl 5,5-diaryl-2-methyl-4,5-dihydrofuran-3-carboxylates **9a$_n$-9c$_n$**.

Compound **9a$_2$** could formally be derived from **7a$_2$**. When compound **7a$_2$** was heated in acetic acid containing a small amount of manganese(II) acetate tetrahydrate for 2 hours, **9a$_2$** was obtained in a 57% yield along with benzophenone (20%) and 2-acetoxyethyl 2-methyl-5,5-diphenyl-4,5-dihydrofuran-3-carboxylate (9%). The latter could be formed by a treatment

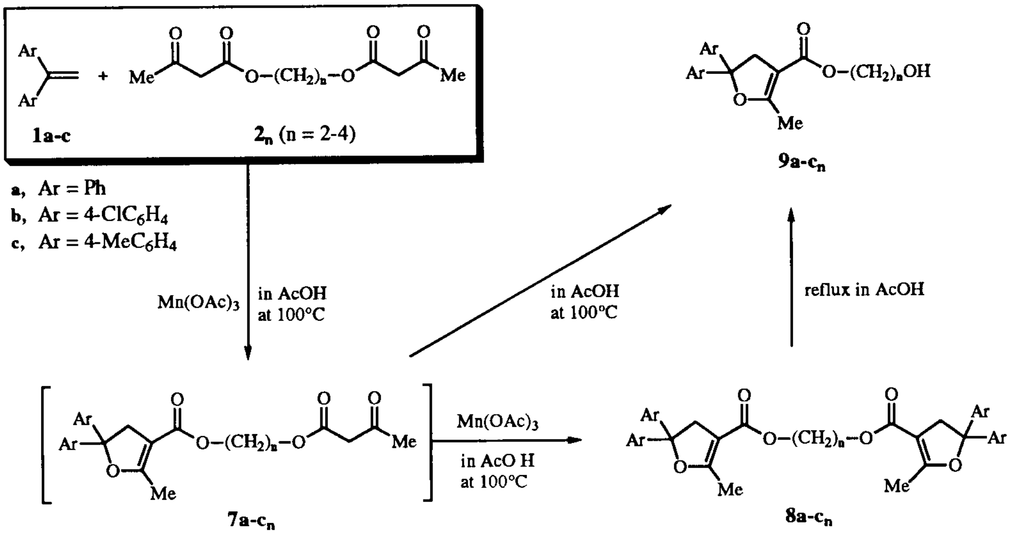
Table 3

Reaction of 1,1-Diphenylethene (**1a**) with Ethylene Di(3-oxobutanoate) (**2$_2$**) in the Presence of Other Metal Oxidants in Acetic Acid at 23°C [a]

Entry	Oxidant	Recovery/%		Product composition (yield/%) [b]						
		1a	**2$_2$**							
24	KMnO$_4$				**4a$_2$** (5)	**5a$_2$** (8)		**9a$_2$** (7)	**10a** (14)	**11a** (18)
25	Co(OAc)$_3$			**3a$_2$** (12)	**4a$_2$** (5)	**5a$_2$** (4)			**10a** (28)	**11a** (25)
26	CAN				**4a$_2$** (12)	**5a$_2$** (25)	**6a$_2$** (10)	**9a$_2$** (7)		
27	CrO$_3$		27						**10a** (55)	**11a** (25)
28	Ni(OAc)$_2$	100	30							
29	Cu(OAc)$_2$	100	30							

[a] Reactions were carried out at a molar ratio of 1:1.5:1 for **1a**:**2$_2$**:oxidant at 23° for 24 hours. [b] All the yields are given for the chromatographically purified materials based on **1a** used.

Scheme 2



of $9a_2$ with acetic acid. Treatment of $8a_2$ under similar reaction conditions also gave $9a_2$, but in a poor yield (11%).

Reactions with potassium permanganate, cobalt(III) acetate, ammonium cerium(IV) nitrate, chromium(VI) oxide, nickel(II) acetate, and copper(II) acetate were examined. Some of $3a_2$, $4a_2$, $5a_2$, $6a_2$, $9a_2$, benzophenone (**10a**), and 2-hydroxy-2,2-diphenylethyl acetate (**11a**) were obtained in the reactions with potassium permanganate, cobalt(III) acetate, or ammonium cerium(IV) nitrate, but in poor yields (Table 3, entries 24-27).

Reactions of $3a_2$ and $7a_2$ with 1,1-Diphenylethene (1a) in the Presence of Manganese(III) Acetate.

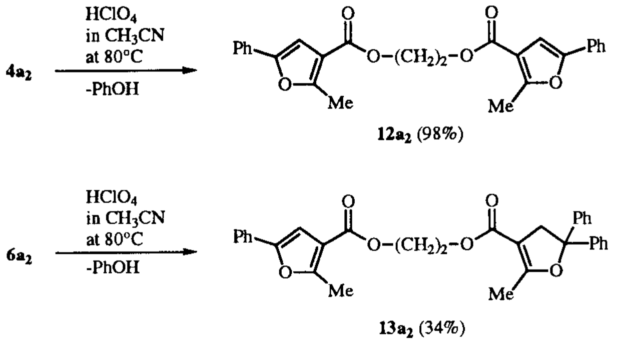
The presence of one remaining active methylene in compounds $3a_2$ and $7a_2$ make possible the formation of another 1,2-dioxane or 4,5-dihydrofuran ring by the reaction with alkene in the presence of manganese(III) acetate and oxygen. The reactions of $3a_2$ and **1a** with manganese(III) acetate in acetic acid at 23° yielded $4a_2$ and $5a_2$, and at 100° gave $6a_2$ and $8a_2$ (see Scheme 1). The reactions of $7a_2$ and **1a** at 23° gave $6a_2$ and $9a_2$ and at 100° under argon atmosphere gave $8a_2$ and $9a_2$ (see Scheme 2).

Acid-Catalyzed Decomposition of $4a_2$ and $6a_2$.

The acid-catalyzed decomposition of 4-acetyl-6,6-diaryl-3-methyl-1,2-dioxan-3-ols was reported to give 2,3,5-trisubstituted furans [7]. In order to prepare a di(furan-3-carboxylate) ester and a compound bearing a furan and a 4,5-dihydrofuran ring, the reactions of $4a_2$ and $6a_2$ were carried out with perchloric acid in acetonitrile. Compound $4a_2$ gave ethylene di(2-methyl-5-phenylfuran-3-carboxylate) ($12a_2$). Similarly, compound $6a_2$ yielded ethylene (2-methyl-5-phenylfuran-3-carboxylate) (2-methyl-5,5-diphenyl-4,5-dihydrofuran-3-carboxylate) ($13a_2$). Phenol was also obtained, but the yield of phenol was not recorded because of its considerable loss during the working-up procedure.

$$\underset{(42\%)}{4a_2} + \underset{(22\%)}{5a_2} \xleftarrow[\text{Mn(OAc)}_3 \text{ in AcOH under dry air}]{\text{at } 23^\circ\text{C}} 1a + 3a_2 \xrightarrow[\text{Mn(OAc)}_3 \text{ in AcOH under argon}]{\text{at } 100^\circ\text{C}} \underset{(48\%)}{6a_2} + \underset{(30\%)}{8a_2}$$

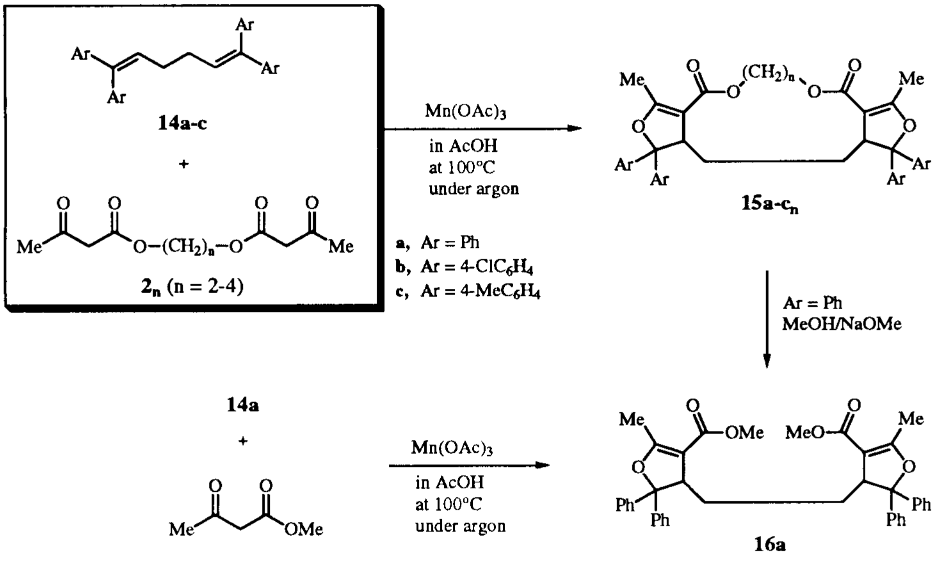
$$\underset{(69\%)}{6a_2} + \underset{(31\%)}{9a_2} \xleftarrow[\text{Mn(OAc)}_3 \text{ in AcOH under dry air}]{\text{at } 23^\circ\text{C}} 1a + 7a_2 \xrightarrow[\text{Mn(OAc)}_3 \text{ in AcOH under argon}]{\text{at } 100^\circ\text{C}} \underset{(71\%)}{8a_2} + \underset{(25\%)}{9a_2}$$



Reaction of Oligomethylene Di(3-oxobutanoate)s 2_n with 1,1,6,6-Tetraaryl-1,5-hexadienes 14a-c in the Presence of Manganese(III) Acetate.

We reported that the reaction of ethyl acetoacetate with 1,1,6,6-tetraaryl-1,5-hexadiene **14a-c** gave 4,4'-ethylenedi(2-methyl-5,5-diphenyl-4,5-dihydrofuran)s [8]. If a similar reaction occurs in the reaction of 2_n and **14a-c**, it would give a macrocyclic diester bearing two 4,5-dihydrofuran rings. This proved to be the case (Scheme 3). The reactions of 2_2-2_4 with **14a-c** were carried out in

Scheme 3



acetic acid at 100° for 45 minutes in the presence of manganese(III) acetate that gave macrocyclic diesters **15a**$_{2\text{-}4}$, **15b**$_2$, and **15c**$_2$ in yields shown in Table 4.

Table 4

Reaction of Oligomethylene Di(3-oxobutanoate)s **2**$_n$ with 1,1,6,6-Tetraaryl-1,5-hexadienes **14a-c** in the Presence of Manganese(III) Acetate in Acetic Acid at 100°C [a]

Entry	Substrate	Product (yield/%) [b]
30	**14a**, **2**$_2$	**15a**$_2$ (40)
31	**14a**, **2**$_3$	**15a**$_3$ (37)
32	**14a**, **2**$_4$	**15a**$_4$ (44)
33	**14b**, **2**$_2$	**15b**$_2$ (24)
34	**14c**, **2**$_2$	**15c**$_2$ (44)

[a] Reactions were carried out at a molar ratio of 1:1.5:7 for 14:**2**$_n$:manganese(III) acetate for 45 minutes. [b] All the yields are given for the chromatographically purified materials based on the alkene used.

The ^{13}C nmr spectrum of compound **15a**$_2$ showed some interesting structural features. It exhibited three methyl carbon signals at δ = 14.1, 14.3, and 14.5, and also three methylene carbons at δ = 22.6, 26.9, and 31.5. A carbonyl carbon and vinyl carbon attached to the oxygen appeared as paired peaks, respectively, but only four peaks were observed for a methine carbon (δ = 51.6), an *O*-methylene carbon (δ = 51. 2), a quaternary carbon (δ = 94.9), and other vinylic carbon (δ = 107.4). A complex aromatic carbon signals also appeared at the lower field. These data indicate that the compound **15a**$_2$ consists of two diastereomers because both contained a stereocenter in each 4,5-dihydrofuran moiety and thus *racemic*- and *meso*-forms are possible. In fact, two peaks were observed in the hplc. Treatment of **15a**$_2$ with methanol-sodium methoxide gave a dimethyl ester **16a** (Scheme 3). The ^{13}C nmr spectrum of **16a** also exhibited two peaks for two methylene carbons and two peaks for methine carbons, indicating that **16a** consists of two stereoisomers.

Inspection of molecular models for the two stereoisomers of compound **15a**$_2$ visualized by MM2 calculations revealed that the two methyl groups in each diastereomer may not be equivalent and thus appeared as three peaks with another overlapped to one of them. The signals for two methylene groups between two 4,5-dihydrofuran rings could also be explained in a similar manner.

The reaction of **14a** with **2**$_2$ at room temperature gave an intractable mixture which could not be separated.

It is thus concluded that the manganese(II and III)-mediated reaction of alkenes, β-keto esters, and oxygen gives the esters of α,ω-alkanediol and 3-hydroxy-1,2-dioxane-4-carboxylic acids in moderate yields, and the reaction at elevated temperature yields the esters of α,ω-alkanediol and 4,5-dihydrofuran-3-carboxylic acids. A combination of the reactions at room temperature and at elevated temperature, and also the acid-catalyzed decomposition of 1,2-dioxane ring make it possible to prepare compounds bearing two 1,2-dioxane, 4,5-dihydrofuran, or furan rings. The reaction of 1,1,6,6-tetraaryl-1,5-hexadienes with oligomethylene di(3-oxobutanoate) in the presence of manganese(III) acetate yielded macrocyclic diesters bearing two 4,5-dihydrofuran rings.

EXPERIMENTAL

Measurements.

All of the ^{1}H and ^{13}C nmr spectra were taken with a JNM PMX-60SI (60 MHz) and a JNM EX-90FT nmr (90 MHz for ^{1}H and 22.5 MHz for ^{13}C) spectrometer with tetramethylsilane being used as the internal standard. Chemical shifts are shown in δ values (ppm). The ir spectra were measured on a JASCO A-102 ir spectrometer and expressed in ν values (cm^{-1}). Mass spectra were taken with a JMS-LX1000 mass spectrometer. The hplc was performed by a Hitachi L-6200 liquid chromatograph equipped with a Wakosil-II 5C18 HG column of 4.6 mm in diameter and 250 mm in length. All of the melting points were determined with a Yanagimoto micromelting-point apparatus MP-J3. Elemental analyses were performed by the Microanalytical Center, Kyushu University, Fukuoka.

Materials.

Manganese(III) acetate dihydrate [9] was prepared according to the method in the literature. 1,1-Diarylethenes **1a-c** were prepared by dehydration of the corresponding alcohols which were synthesized from substituted acetophenones and arylmagnesium bromides [10]. Oligomethylene di(3-oxobutanoate)s $\mathbf{2}_{2\text{-}4}$ were prepared by the reaction of the corresponding α,ω-alkanediols with diketene [11]. 1,1,6,6-Tetraaryl-1,5-hexadienes **14a-c** were synthesized from diethyl adipate and arylmagnesium bromides [12].

Reaction of 1,1-Diarylethenes **1a-c** with Oligomethylene Di(3-oxobutanoate)s $\mathbf{2}_n$ and Oxygen in the Presence of Various Metal Salts at Room Temperature.

The general procedure for the reaction of 1,1-diarylethene **1a-c** with oligomethylene di(3-oxobutanoate)s $\mathbf{2}_n$ in the presence of a metal salt was as follows. A metal salt (1 mmole) or a mixture of manganese(II) acetate (1 mmole) and manganese(III) acetate (0.2 mmole) was added to a stirred solution of an alkene (1 mmole) and $\mathbf{2}_n$ (0.5-3 mmoles) in acetic acid (30 ml) in a three-necked flask equipped with a dry-air inlet tube. The mixture was stirred at 23° for the period of time shown in Tables 1 and 3. The reaction was quenched by adding water (60 ml) and the mixture was then extracted with benzene. After removing the benzene, the resulting products were separated on tlc (Wakogel B10) while eluting with a mixture of hexane-ethyl acetate (1:1 v/v). The products were further purified for analytical samples by recrystallization from appropriate solvents. The yields are listed in Tables 1 and 3. Specific details are given below.

Products.

2-(3-Oxobutanoyloxy)ethyl 3-Hydroxy-3-methyl-6,6-diphenyl-1,2-dioxane-4-carboxylate ($\mathbf{3a}_2$).

This compound had mp 110-111° (from benzene-hexane); ir (chloroform): ν = 3700-3300, 1745, 1722, 1658 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ = 1.35 (3H, s), 2.15 (3H, s), 2.83 (3H, s), 3.40 (2H, s), 3.93 (1H, s), 4.30 (4H, s), 7.10-7.70 (10H, m); ^{13}C nmr (deuteriochloroform): δ = 203.7, 171.0, 166.8, 143.3, 140.8, 128.5, 128.4, 128.0, 127.4, 126.8, 125.8, 98.5, 85.2, 62.7, 62.5, 49.8, 45.7, 31.6, 30.3, 24.4.

Anal. Calcd. for $C_{24}H_{26}O_8$: C, 65.15; H, 5.92. Found: C, 65.02; H, 5.94.

Ethylene Di(3-hydroxy-3-methyl-6,6-diphenyl-1,2-dioxane-4-carboxylate) ($\mathbf{4a}_2$).

This compound had mp 122-124° (from benzene-hexane); ir (chloroform): ν = 3700-3200, 1750 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ = 1.30 (6H, s), 2.85 (6H, s), 3.75 (1H, s), 3.85 (1H, s), 4.30 (4H, s), 7.30-7.70 (20H, m); ^{13}C nmr (deuteriochloroform): δ = 170.8, 170.7, 143.2, 140.7, 128.5, 128.4, 128.1, 127.4, 126.7, 125.7, 98.6, 85.2, 62.5, 45.7, 31.3, 24.3.

Anal. Calcd. for $C_{38}H_{38}O_{10}$: C, 69.71; H, 5.85. Found: C, 69.82; H, 5.94.

Ethylene Di[6,6-bis(4-chlorophenyl)-3-hydroxy-3-methyl-1,2-dioxane-4-carboxylate] ($\mathbf{4b}_2$).

This compound had mp 189-190° (from benzene-hexane); ir (chloroform): ν = 3704, 1736 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ = 1.40 (6H, s), 2.80 (6H, s), 3.50-4.00 (2H, br s), 4.40 (4H, s), 7.25-7.40 (16H, m).

Anal. Calcd. for $C_{38}H_{34}O_{10}Cl_4$: C, 57.59; H, 4.32. Found: C, 57.40; H, 4.51.

Ethylene Di[3-hydroxy-3-methyl-6,6-bis(4-methylphenyl)-1,2-dioxane-4-carboxylate] ($\mathbf{4c}_2$).

This compound had mp 107-109° (from benzene-hexane); ir (chloroform): ν = 3592, 1738 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ = 1.40 (6H, s), 2.25 (6H, s), 2.43 (6H, s), 2.85 (6H, s), 3.50-4.10 (2H, br s), 4.36 (4H, s), 7.13-7.53 (16H, m).

Anal. Calcd. for $C_{42}H_{46}O_{10}$: C, 70.97; H, 6.52. Found: C, 70.90; H, 6.56.

Trimethylene Di(3-hydroxy-3-methyl-6,6-diphenyl-1,2-dioxane-4-carboxylate) ($\mathbf{4a}_3$).

This compound had mp 99-101° (from benzene-hexane); ir (chloroform): ν = 3592, 1729 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ = 1.40 (6H, s), 2.03 (2H, q, J = 8 Hz), 2.88 (6H, s), 3.60-4.10 (2H, br s), 4.27 (4H, t, J = 8 Hz), 7.10-7.70 (20H, m).

Anal. Calcd. for $C_{39}H_{40}O_{10}$: C, 70.05; H, 6.03. Found: C, 70.01; H, 6.10.

Tetramethylene Di(3-hydroxy-3-methyl-6,6-diphenyl-1,2-dioxane-4-carboxylate) ($\mathbf{4a}_4$).

This compound had mp 101-103° (from benzene-hexane); ir (chloroform): ν = 3595, 1725 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ = 1.40 (6H, s), 1.70 (4H, m), 2.83 (6H, s), 3.60-4.00 (2H, br s), 4.15 (4H, m), 6.95-7.70 (20H, m).

Anal. Calcd. for $C_{40}H_{42}O_{10}$: C, 70.37; H, 6.20. Found: C, 70.58; H, 6.34.

2-Hydroxyethyl 3-Hydroxy-3-methyl-6,6-diphenyl-1,2-dioxane-4-carboxylate ($\mathbf{5a}_2$).

This compound had mp 117-119° (from benzene-hexane); ir (chloroform): ν = 3412, 1728 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ = 1.35 (3H, s), 2.05-2.50 (1H, s), 2.92 (3H, s), 3.65-3.85 (2H, m), 3.90-4.10 (1H, br s), 4.25-4.32 (2H, m), 7.30-7.70 (10H, m); ^{13}C nmr (deuteriochloroform): δ = 171.4, 143.2, 140.7, 128.6, 128.4, 128.1, 127.5, 126.7, 125.9, 98.7, 85.3, 66.6, 60.9, 45.8, 31.6, 24.5.

Anal. Calcd. for $C_{20}H_{22}O_6$: C, 67.03; H, 6.19. Found: C, 66.72; H, 6.14.

2-Hydroxyethyl 6,6-Bis(4-chlorophenyl)-3-hydroxy-3-methyl-1,2-dioxane-4-carboxylate ($\mathbf{5b}_2$).

This compound was obtained as a colorless liquid; ir (chloroform): ν = 3460, 1731 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ = 1.40 (3H, s), 2.10-2.35 (1H, br s), 2.85 (3H, s), 3.50-3.75 (1H, br s), 3.77 (2H, m), 4.30 (2H, m), 7.25-7.40 (8H, m); ^{13}C nmr (deuteriochloroform): δ = 171.1, 141.2, 138.9, 134.3, 133.7, 128.9, 128.7, 128.2, 127.3, 98.7, 84.6, 66.6, 60.7, 45.7, 31.3, 24.5; ms: FAB (positive ion) m/z = 409, 319, 192, 111; (negative ion) m/z = 425 (M$^-$ -1), 347, 305, 249, 153.

2-Hydroxyethyl 3-Hydroxy-3-methyl-6,6-bis(4-methylphenyl)-1,2-dioxane-4-carboxylate ($\mathbf{5c}_2$).

This compound was obtained as a colorless liquid; ir (chloroform): ν = 3592, 3448, 1728 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ = 1.40 (3H, s), 2.10-2.50 (1H, br s), 2.23 (3H, s), 2.30 (3H, s), 2.85 (3H, s), 3.20-3.70 (1H, br s), 3.75 (2H, m), 4.25 (2H, m), 7.13-7.53 (8H, m); ^{13}C nmr (deuteriochloroform): δ = 171.4, 140.4, 137.9, 137.8, 137.0, 129.2, 129.0, 126.6, 125.8, 98.6, 85.2, 66.6, 60.8, 45.9, 31.5, 24.5, 21.0; ms: FAB (positive ion) m/z = 369, 279, 261, 211, 119, 91; (negative ion) m/z = 385 (M$^-$ -1), 372, 341, 307, 209, 153.

3-Hydroxypropyl 3-Hydroxy-3-methyl-6,6-diphenyl-1,2-dioxane-4-carboxylate (**5a**$_3$).

This compound had mp 86-88° (from benzene-hexane); ir (chloroform): ν = 3476, 1728 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ = 1.40 (3H, s), 1.88 (2H, m), 2.20-2.40 (1H, br s), 2.87 (3H, s), 3.60-3.90 (1H, br s), 3.75 (2H, t, J = 6 Hz), 4.30 (2H, t, J = 6 Hz), 7.20-7.80 (10H, m).

Anal. Calcd. for $C_{21}H_{24}O_6$: C, 67.73; H, 6.49. Found: C, 67.52; H, 6.46.

4-Hydroxybutyl 3-Hydroxy-3-methyl-6,6-diphenyl-1,2-dioxane-4-carboxylate (**5a**$_4$).

This compound had mp 70-73° (from benzene-hexane); ir (chloroform): ν = 3495, 1726 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ = 1.40 (3H, s), 1.70 (4H, m), 2.20-2.40 (1H, br s), 2.85 (3H, s), 3.50-4.00 (1H, br s), 3.67 (2H, m), 4.20 (2H, m), 7.30-7.60 (10H, m).

Anal. Calcd. for $C_{22}H_{26}O_6$: C, 68.37; H, 6.78. Found: C, 67.96; H, 6.72.

Ethylene (3-Hydroxy-3-methyl-6,6-diphenyl-1,2-dioxane-4-carboxylate) (2-Methyl-5,5-diphenyl-4,5-dihydrofuran-3-carboxylate) (**6a**$_2$).

This compound had mp 137-139° (from benzene-hexane); ir (chloroform): ν = 3700-3250, 1740, 1695 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ = 1.37 (3H, s), 2.32 (3H, t, J = 1.6 Hz), 2.85 (3H, s), 3.50-3.90 (1H, br s), 3.50-3.65 (2H, q, J = 1.6 Hz), 4.37 (4H, s), 7.30-7.50 (20H, m); ^{13}C nmr (deuteriochloroform): δ = 171.0, 167.6, 165.3, 145.0, 143.2, 140.8, 128.5, 128.4, 128.0, 127.6, 127.4, 126.7, 125.8, 125.7, 101.2, 98.5, 92.0, 85.2, 63.2, 61.0, 45.6, 43.9, 31.6, 24.4, 14.3.

Anal. Calcd. for $C_{38}H_{36}O_8$: C, 73.53; H, 5.85. Found: C, 73.57; H, 5.83.

Ethylene [3-Hydroxy-3-methyl-6,6-bis(4-methylphenyl)-1,2-dioxane-4-carboxylate] [2-Methyl-5,5-bis(4-methylphenyl)-4,5-dihydrofuran-3-carboxylate] (**6c**$_2$).

This compound had mp 153-155° (from benzene-hexane); ir (chloroform): ν = 3592, 1740, 1695 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ = 1.37 (3H, s), 2.23 (3H, t, J = 1.6 Hz), 2.30 (12H, s), 2.82 (3H, s), 3.53 (2H, q, J = 1.6 Hz), 3.60-3.80 (1H, br s), 4.33 (4H, s), 7.10-7.40 (16H, m).

Anal. Calcd. for $C_{42}H_{44}O_8$: C, 74.53; H, 6.55. Found: C, 74.53; H, 6.57.

Trimethylene (3-Hydroxy-3-methyl-6,6-diphenyl-1,2-dioxane-4-carboxylate) (2-Methyl-5,5-diphenyl-4,5-dihydrofuran-3-carboxylate) (**6a**$_3$).

This compound was obtained as a colorless liquid; ir (chloroform): ν = 3596, 1729, 1695 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ = 1.40 (3H, s), 2.03 (2H, m), 2.35 (3H, t, J = 1.6 Hz), 2.85 (3H, s), 3.60 (2H, q, J = 1.6 Hz), 3.90-4.20 (1H, br s), 4.30 (4H, m), 7.20-7.75 (20H, m); ^{13}C nmr (deuteriochloroform): δ = 171.3, 167.0, 165.6, 145.0, 143.3, 140.8, 128.5, 128.4, 127.9, 127.6, 127.4, 126.7, 125.8, 125.7, 101.4, 98.5, 91.8, 85.2, 61.9, 60.0, 58.3, 45.7, 44.0, 31.6, 24.5, 14.3; ms: FAB (positive ion) m/z = 635 (M$^+$ +1), 601, 553, 523, 461, 363, 321, 263, 105, 77.

Tetramethylene (3-Hydroxy-3-methyl-6,6-diphenyl-1,2-dioxane-4-carboxylate) (2-Methyl-5,5-diphenyl-4,5-dihydrofuran-3-carboxylate) (**6a**$_4$).

This compound had mp 94-96° (from benzene-hexane); ir (chloroform): ν = 3592, 1728, 1687 cm^{-1}; ^{1}H nmr (deuteriochloroform) δ 1.40 (3H, s), 1.75 (4H, m), 2.45 (3H, t, J = 1.6 Hz), 2.90 (3H, s), 3.65 (2H, q, J = 1.6 Hz), 3.90-4.20 (1H, br s), 4.20 (4H, m), 7.35-7.75 (20 H, m).

Anal. Calcd. for $C_{40}H_{40}O_8$: C, 74.06; H, 6.21. Found: C, 73.86; H, 6.20.

3-Hydroxypropyl 2-Methyl-5,5-diphenyl-4,5-dihydrofuran-3-carboxylate (**9a**$_3$).

This compound was obtained as a colorless liquid; ir (chloroform): ν = 3500, 1686, 1648 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ = 1.87 (2H, m), 2.15-2.45 (1H, br s), 2.33 (3H, t, J = 1.6 Hz), 3.60-3.80 (4H, m), 4.30 (2H, t, J = 6.4 Hz), 7.40 (10H, m); ^{13}C nmr (deuteriochloroform): δ = 167.0, 166.2, 145.1, 128.4, 127.6, 125.7, 101.4, 91.7, 60.5, 59.2, 44.1, 32.1, 14.3; ms: FAB (positive ion) m/z = 339 (M$^+$ +1), 321, 263, 65.

4-Hydroxybutyl 2-Methyl-5,5-diphenyl-4,5-dihydrofuran-3-carboxylate (**9a**$_4$).

This compound was obtained as a colorless liquid; ir (chloroform): ν = 3500, 1683, 1648 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ = 1.67 (4H, m), 2.25-2.40 (1H, br s), 2.33 (3H, t, J = 1.6 Hz), 3.55-3.75 (4H, m), 4.15 (2H, t, J = 6.4 Hz), 7.40 (10H, m); ^{13}C nmr (deuteriochloroform): δ = 166.5, 165.8, 145.2, 128.4, 127.5, 125.7, 101.7, 91.6, 63.5, 62.4, 44.1, 29.3, 25.3, 14.3; ms: FAB (positive ion) m/z = 353 (M$^+$ +1), 335, 279, 263, 247, 234, 220, 191, 105, 77.

Benzophenone (**10a**).

This compound had mp 48° (from ethanol) [13].

4,4'-Dichlorobenzophenone (**10b**).

This compound had mp 144-145° (from benzene-hexane) [14].

2-Hydroxy-2,2-diphenylethyl Acetate (**11a**).

This compound had mp 92-93° (from ethanol) [15].

2,2-Bis(4-chlorophenyl)-2-hydroxyethyl Acetate (**11b**).

This compound had mp 95-96° [2].

Treatments of **3a**$_2$ and **4a**$_2$ with Aqueous Acetic Acid.

A mixture of **3a**$_2$ (221 mg) and manganese(II) acetate tetrahydrate (245 mg) in acetic acid (10 ml) was stirred at 23° for 24 hours, and the mixture was worked up in a similar manner that was described previously, giving **5a**$_2$ (30 mg, 19%). The treatment of **4a**$_2$ (90 mg) with manganese(II) acetate tetrahydrate (33 mg) in acetic acid (10 ml) under the same reaction conditions yielded **5a**$_2$ (3 mg, 6%).

Reactions of 1,1-Diarylethene **1a-c** with Oligomethylene Di(3-oxobutanoate) **2**$_n$ in the Presence of Manganese(III) Acetate at Elevated Temperature.

The general procedure for the reaction of 1,1-diarylethene **1a-c** with oligomethylene di(3-oxobutanoate)s **2$_n$** in the presence of manganese(III) acetate was as follows. Manganese(III) acetate (1.5-3.5 mmoles) was added to a stirred solution of an alkene (1 mmole) and oligomethylene di(3-oxobutanoate) **2$_n$** (0.5-2.0 mmoles) in acetic acid (30 ml) at 100° under an atmosphere of argon. The reaction mixture was heated at the same temperature until the dark-brown color of the solution turned opaque white. After the solvent was removed under reduced pressure, the residue was triturated with water and extracted with benzene. The products were separated on tlc (Wakogel B10) while eluting with a mixture of diethyl ether-hexane (8:2 v/v). The product yields are listed in Table 2.

2-(3-Oxobutanoyloxy)ethyl 2-Methyl-5,5-diphenyl-4,5-dihydrofuran-3-carboxylate (**7a$_2$**).

This compound was obtained as a colorless liquid; ir (chloroform): ν = 1750, 1718, 1695 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ = 2.20 (3H, s), 2.35 (3H, t, J = 1.6 Hz), 3.45 (2H, s), 3.60 (2H, q, J = 1.6 Hz), 4.35 (4H, s), 7.25-7.50 (10H, m); ^{13}C nmr (deuteriochloroform): δ = 199.9, 167.3, 166.8, 165.1, 144.9, 128.3, 127.5, 125.6, 101.2, 91.8, 63.1, 61.0, 49.7, 43.8, 30.0, 14.2; ms: FAB (positive ion) m/z = 409 (M$^+$ +1), 307, 263, 191, 129, 85.

Ethylene Di(2-methyl-5,5-diphenyl-4,5-dihydrofuran-3-carboxylate) (**8a$_2$**).

This compound had mp 159-160° (from benzene-hexane); ir (chloroform): ν = 1695 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ = 2.30 (6H, t, J = 1.6 Hz), 3.60 (4H, q, J = 1.6 Hz), 4.35 (4H, s), 7.25-7.50 (20H, m); ^{13}C nmr (deuteriochloroform): δ = 167.0, 165.3, 145.0, 128.3, 127.5, 125.6, 101.4, 91.8, 61.6, 44.0, 14.3.

Anal. Calcd. for $C_{38}H_{34}O_6$: C, 77.80; H, 5.84. Found: C, 77.90; H, 5.90.

Ethylene Di[5,5-bis(4-chlorophenyl)-2-methyl-4,5-dihydrofuran-3-carboxylate] (**8b$_2$**).

This compound was obtained as a colorless liquid; ir (chloroform): ν = 1691, 1650 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ = 2.25 (6H, t, J = 1.6 Hz), 3.50 (4H, q, J = 1.6 Hz), 4.35 (4H, s), 7.35 (16H, s); ^{13}C nmr (deuteriochloroform): δ = 166.7, 165.0, 143.1, 133.8, 128.7, 127.0, 101.5, 90.8, 61.7, 43.9, 14.2; ms: FAB (positive ion) m/z = 726 (M$^+$ +2), 375, 331, 141, 139, 111.

Ethylene Di[2-methyl-5,5-bis(4-methylphenyl)-4,5-dihydrofuran-3-carboxylate] (**8c$_2$**).

This compound had mp 140-141° (from benzene-hexane); ir (chloroform): ν = 1690, 1647 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ = 2.30 (18H, s), 3.50 (4H, q, J = 1.7 Hz), 4.25 (4H, s), 7.15 (16H, m).

Anal. Calcd. for $C_{42}H_{42}O_6$: C, 78.48; H, 6.59. Found: C, 78.76; H, 6.65.

Trimethylene Di(2-methyl-5,5-diphenyl-4,5-dihydrofuran-3-carboxylate) (**8a$_3$**).

This compound was obtained as a colorless liquid; ir (chloroform): ν = 1685 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ = 1.97 (2H, t, J = 6.4 Hz), 2.33 (6H, t, J = 1.4 Hz), 3.60 (4H, q, J = 1.4 Hz), 4.20 (4H, t, J = 6.4 Hz), 7.40 (20H, m); ^{13}C nmr (deuteriochloroform): δ = 166.7, 165.6, 145.1, 128.3, 127.5, 125.7, 101.5, 91.7, 60.4, 44.1, 28.4, 14.3; ms: FAB (positive ion) m/z = 602 (M$^+$ +2), 321, 263, 191, 105.

Tetramethylene Di(2-methyl-5,5-diphenyl-4,5-dihydrofuran-3-carboxylate) (**8a$_4$**).

This compound had mp 68-70° (from benzene-hexane); ir (chloroform): ν = 1685, 1649 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ = 1.70 (4H, m), 2.33 (3H, t, J = 1.6 Hz), 3.60 (2H, q, J = 1.6 Hz), 4.17 (4H, m), 7.40 (20H, m); ^{13}C nmr (deuteriochloroform): δ = 166.4, 165.6, 145.1, 128.3, 127.5, 125.6, 101.6, 91.6, 63.2, 44.1, 25.6, 14.2; ms: FAB (positive ion) m/z = 615 (M$^+$ +1), 601, 335, 279, 263, 247, 233, 221, 191, 105, 77.

Anal. Calcd. for $C_{40}H_{38}O_6$: C, 78.23; H, 6.38. Found: C, 78.15; H, 6.23.

2-Hydroxyethyl 2-Methyl-5,5-diphenyl-4,5-dihydrofuran-3-carboxylate (**9a$_2$**).

This compound was obtained as a colorless liquid; ir (chloroform): ν = 3642, 1695 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ = 1.95-2.25 (1H, br s), 2.33 (3H, t, J = 1.6 Hz), 3.60 (2H, q, J = 1.6 Hz), 3.85 (2H, m), 4.30 (2H, m), 7.40 (10H, m); ^{13}C nmr (deuteriochloroform): δ = 167.5, 166.2, 145.0, 128.4, 127.6, 125.7, 101.3, 91.9, 65.6, 61.6, 44.0, 14.4; ms: FAB (positive ion) m/z = 325 (M$^+$ +1), 307, 263, 191, 105.

2-Hydroxyethyl 5,5-Bis(4-chlorophenyl)-2-methyl-4,5-dihydrofuran-3-carboxylate (**9b$_2$**).

This compound was obtained as a colorless liquid; ir (chloroform): ν = 3628, 1690, 1649 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ = 2.00-2.45 (1H, br s), 2.33 (3H, t, J = 1.6 Hz), 3.58 (2H, q, J = 1.6 Hz), 3.90 (2H, m), 4.30 (2H, m), 7.30 (8H, m); ^{13}C nmr (deuteriochloroform): δ = 167.1, 165.9, 143.1, 133.8, 128.7, 127.1, 101.4, 90.9, 65.8, 61.7, 43.9, 14.3; ms: FAB (positive ion) m/z = 393 (M$^+$ +1), 331, 141, 139, 111, 87.

2-Hydroxyethyl 2-Methyl-5,5-bis(4-methylphenyl)-4,5-dihydrofuran-3-carboxylate (**9c$_2$**).

This compound was obtained as a colorless liquid; ir (chloroform): ν = 3460, 1687, 1644 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ = 1.75-2.15 (1H, br s), 2.33 (9H, s), 3.60 (2H, q, J = 1.6 Hz), 3.85 (2H, m), 4.27 (2H, m), 7.25 (8H, m); ^{13}C nmr (deuteriochloroform): δ = 167.5, 166.3, 142.3, 137.3, 129.0, 125.6, 101.2, 91.9, 65.6, 61.7, 44.0, 21.0, 14.4; ms: FAB (positive ion) m/z = 353 (M$^+$ + 1), 335, 291, 249, 219, 119.

3-Hydroxypropyl 2-Methyl-5,5-diphenyl-4,5-dihydrofuran-3-carboxylate (**9a$_3$**) (*vide supra*).

4-Hydroxybutyl 2-Methyl-5,5-diphenyl-4,5-dihydrofuran-3-carboxylate (**9a$_4$**) (*vide supra*).

Treatment of **7a$_2$** and **8a$_2$** with Aqueous Acetic Acid.

A mixture of **7a$_2$** (121 mg) and manganese(II) acetate tetrahydrate (123 mg) in acetic acid (10 ml) was stirred at 100° for 2 hours, and the products were separated on tlc giving **9a$_2$** (55 mg, 57%), **10a** (11 mg, 20%), and 2-acetoxyethyl 2-methyl-5,5-diphenyl-4,5-dihydrofuran-3-carboxylate (10 mg, 9%). This compound was obtained as a colorless liquid; ir (chloroform): ν = 1737, 1691, 1649 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ = 2.03 (3H, s), 2.33 (3H, t, J = 1.6 Hz), 3.60 (2H, q, J = 1.6 Hz), 4.30 (4H, s), 7.25-7.50 (10H, m); ^{13}C nmr (deuteriochloroform): δ = 170.8, 167.2, 165.3, 145.1, 128.4, 127.6, 125.7, 101.4, 91.8, 62.4, 61.4, 44.0, 20.8, 14.4.

The treatment of **8a$_2$** (136 mg) with acetic acid (10 ml) containing manganese(II) acetate tetrahydrate (113 mg) at reflux temperature for 6 hours gave **9a**$_2$ (8 mg, 11%).

Reactions of **3a**$_2$ and **7a**$_2$ with 1,1-Diphenylethene (**1a**) in the Presence of Manganese(III) Acetate.

Manganese(III) acetate dihydrate (50 mg) was added to a stirred solution of **1a** (36 mg) and **3a**$_2$ (171 mg) in acetic acid (30 ml) in a three-necked flask equipped with a dry-air inlet tube. The mixture was stirred at 23° under an air stream for 20 hours. After removing the solvent *in vacuo*, the residue was triturated with water and extracted with benzene. The extracts were washed with water, dried (anhydrous sodium sulfate) and evaporated. The residue was purified on tlc (Wakogel B10) eluting with a mixture of ethyl acetate-hexane (1:1 v/v) to give **4a**$_2$ (55 mg, 42%), **5a**$_2$ (20 mg, 22%), and **10a** (5 mg, 14%).

The reaction of **7a**$_2$ (95 mg) with **1a** (16 mg) in the presence of manganese(III) acetate dihydrate (22 mg) at 23° for 23 hours gave **6a**$_2$ (38 mg, 69%) and **9a**$_2$ (15.8 mg, 31%). The reactions of **3a**$_2$ (111 mg) with **1a** (36 mg) and manganese(III) acetate dihydrate (149 mg) at 100° under argon atmosphere for 5 minutes yielded **6a**$_2$ (60 mg, 48%) and **8a**$_2$ (26 mg, 30%), and the reaction of **7a**$_2$ (145 mg) with **1a** (58 mg) and manganese(III) acetate dihydrate (208 mg) under similar reaction conditions gave **8a**$_2$ (133 mg, 71%) and **9a**$_2$ (29 mg, 25%), after working-up in a manner similar to the above.

Acid-Catalyzed Decomposition of **4a**$_2$ and **6a**$_2$.

A solution of **4a**$_2$ (92 mg) in acetonitrile (3 ml) containing 60% perchloric acid (13 mg) was heated at 80° for 20 minutes. The reaction was quenched with water (10 ml), and the reaction mixture was extracted with chloroform (2 x 10 ml). The extract was washed with water, dried (anhydrous magnesium sulfate), and evaporated. The residue was chromatographed on a silica-gel plate while eluting with chloroform to give ethylene di(2-methyl-5-phenylfuran-3-carboxylate) (**12**$_{a2}$) (59 mg, 98%).

This compound had mp 181-183° (from benzene-hexane); ir (chloroform): ν = 1714 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ = 2.65 (6H, s), 4.60 (4H, s), 6.95 (2H, s), 7.30-7.80 (10H, m); ^{13}C nmr (deuteriochloroform): δ = 163.7, 159.1, 152.0, 130.0, 128.8, 127.8, 123.7, 115.0, 105.4, 62.0, 14.0.

Anal. Calcd. for $C_{26}H_{22}O_6$: C, 72.55; H, 5.15. Found: C, 72.74; H, 5.23.

Similarly, a solution of **6a**$_2$ (109 mg) in acetonitrile (5 ml) containing a 60% perchloric acid (15 mg) was heated at 80° for 20 minutes. The reaction was quenched with water (10 ml), and the reaction mixture was extracted with benzene (2 x 10 ml). The extract was washed with water, dried (anhydrous magnesium sulfate), and evaporated. The residue was chromatographed on a silica-gel plate while eluting with chloroform to give ethylene (2-methyl-5-phenylfuran-3-carboxylate) (2-methyl-5,5-diphenyl-4,5-dihydrofuran-3-carboxylate) (**13a**$_2$) (30 mg, 34%).

This compound had mp 131-132° (from methanol); ir (chloroform): ν = 1725, 1716, 1652 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 2.35 (3H, t, J = 1.6 Hz), 2.60 (3H, s), 3.65 (2H, q, J = 1.6 Hz), 4.50 (4H, s), 6.95 (1H, s), 7.30-7.80 (15H, m); ^{13}C nmr (deuteriochloroform): δ = 167.2, 165.3, 163.7, 158.9, 151.9, 145.1, 130.0, 128.7, 128.4, 127.7, 127.6, 125.7, 123.7, 115.0, 105.5, 101.4, 91.9, 62.1, 61.5, 44.0, 14.4, 13.9; ms: FAB (positive ion) m/z = 508 (M$^+$), 307, 263, 229, 185, 105, 77.

Anal. Calcd. for $C_{32}H_{28}O_6$: C, 75.58; H, 5.55. Found: C, 75.71; H, 5.50.

Reaction of Oligomethylene Di(3-oxobutanoate)s **2**$_n$ with 1,1,6,6-Tetraaryl-1,5-hexadienes **14a-c** in the Presence of Manganese(III) Acetate.

A mixture of a 1,1,6,6-tetraaryl-1,5-hexadiene (1 mmole), a oligomethylene di(3-oxobutanoate)s **2**$_n$ (1.5 mmoles), and manganese(III) acetate dihydrate (7 mmoles) in acetic acid (60 ml) was stirred at 100° under an argon atmosphere for 45 minutes. After removal of the solvent under reduced pressure, the residue was triturated with water and then extracted with benzene. The crude products were separated on tlc using a mixture of diethyl ether-hexane (1:1 v/v) as the developing solvent to give the corresponding macrocyclic diester bearing two 4,5-dihydrofuran rings **15a**$_{2\text{-}4}$, **15b**$_2$, and **15c**$_2$ in the yields shown in Table 4.

9,18-Dimethyl-2,7-dioxo-11,11,16,16-tetraphenyl-3,6,10,17-tetraoxatricyclo[13.3.0.0^{8,12}]octadeca-8,18-diene (**15a**$_2$).

This compound had mp 197-199° (from benzene-hexane); ir (chloroform): ν = 1693 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 0.92-1.15(4H,m), 2.23 (3H, s), 2.29 (3H, s), 3.75-3.85 (2H, br s), 4.43 (4H, s), 7.05-7.40 (20H, m); ^{13}C nmr (deuteriochloroform) δ = 166.8, 166.4, 165.5, 165.4, 145.3, 145.0, 141.0, 140.7, 128.3, 128.0, 127.8, 127.6, 127.5, 126.9, 126.6, 126.2, 126.1, 125.9, 107.4, 94.9, 60.8, 51.2, 31.5, 26.9, 22.6, 14.5, 14.3, 14.1.

Anal. Calcd. for $C_{40}H_{36}O_6$: C, 78.41; H, 5.92. Found: C, 78.32; H, 6.03.

11,11,16,16-Tetrakis(4-chlorophenyl)-9,18-dimethyl-2,7-dioxo-3,6,10,17-tetraoxatricyclo[13.3.0.0^{8,12}]octadeca-8,18-diene (**15b**$_2$).

This compound had mp 176-178° (from benzene-hexane); ir (chloroform): ν = 1693 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ = 0.85 (4H, br s), 2.25 (3H, s), 2.30 (3H, s), 3.75 (2H, br s), 4.30 (4H, m), 6.90-7.50 (16H, m); ^{13}C nmr (deuteriochloroform): δ = 166.3, 164.8, 143.6, 139.3, 133.9, 133.0, 128.4, 128.0, 127.4, 127.1, 107.0, 93.2, 61.2, 49.9, 24.4, 14.9.

Anal. Calcd. for $C_{40}H_{32}O_6Cl_4$: C, 64.02; H, 4.30. Found: C, 64.37; H, 4.47.

9,18-Dimethyl-11,11,16,16-tetrakis(4-methylphenyl)-2,7-dioxo-3,6,10,17-tetraoxatricyclo[13.3.0.0^{8,12}]octadeca-8,18-diene (**15c**$_2$).

This compound had mp 125-127° (from benzene-hexane); ir (chloroform): ν = 1692 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ = 0.90-1.17 (4H, br s), 2.20 (3H, s), 2.30 (3H, s), 2.33 (12H, s), 3.70 (2H, br s), 4.40 (4H, s), 6.90-7.40 (16H, m); ^{13}C nmr (deuteriochloroform): δ = 166.9, 166.5, 165.7, 165.6, 142.7, 142.4, 138.5, 138.1, 137.3, 137.2, 136.1, 128.7, 128.3, 126.6, 126.2, 125.8, 107.6, 95.1, 60.8, 50.9, 27.1, 21.1, 21.0, 14.6, 14.4.

Anal. Calcd. for $C_{44}H_{44}O_6$: C, 79.02; H, 6.63. Found: C, 78.70; H, 6.50.

10,19-Dimethyl-2,8-dioxo-12,12,17,17-tetraphenyl-3,7,11,18-tetraoxatricyclo[14.3.0.0^{9,13}]nonadeca-9,19-diene (**15a**$_3$).

This compound had mp 259-260° (from benzene-hexane); ir (chloroform): ν = 1691 cm^{-1}; ^{1}H nmr (deuteriochloroform): δ = 1.10-1.25 (4H, br s), 1.90-2.40 (8H, m), 3.55-3.75 (2H, br s), 4.10-4.70 (4H, m), 6.90-7.60 (20H, m); ^{13}C nmr (deuteriochloroform): δ = 167.5, 166.0, 145.2, 141.0, 128.4, 128.1, 127.8, 127.6, 126.9, 126.7, 126.1, 107.8, 95.3, 63.3, 49.2, 27.9, 27.6, 14.5.

Anal. Calcd. for $C_{41}H_{38}O_6$: C, 78.57; H, 6.11. Found: C, 78.72; H, 6.17.

11,20-Dimethyl-2,9-dioxo-13,13,18,18-tetraphenyl-3,8,12,19-tetraoxatricyclo[15.3.0.0$^{10.14}$]icosa-10,20-diene (**15a$_4$**).

This compound had mp 124-126° (from benzene-hexane); ir (chloroform): $\nu = 1687$ cm^{-1}; ^{1}H nmr (deuteriochloroform): $\delta =$ 1.05 (4H, br s), 1.80-1.90 (4H, m), 2.18 (3H, s), 2.27 (3H, s), 3.65 (2H, br s), 4.30 (4H, m), 6.90-7.70 (20H, m); ^{13}C nmr (deuteriochloroform): $\delta =$ 165.9, 165.8, 165.6, 145.5, 145.2, 141.1, 140.9, 128.0, 127.8, 127.6, 127.5, 126.7, 126.5, 126.1, 125.9, 107.8, 107.5, 94.7, 94.5, 63.1, 62.7, 50.3, 49.1, 27.6, 26.1, 25.5, 14.8, 14.5.

Anal. Calcd. for $C_{42}H_{40}O_6$: C, 78.73; H, 6.29. Found: C, 78.35; H, 6.16.

Preparation of 4,4'-Ethylenedi(3-methoxycarbonyl-2-methyl-5,5-diphenyl-4,5-dihydrofuran) (**16a**).

Compound **16a** was prepared in the following ways. a) To a solution of sodium methoxide (0.96 mmole) in anhydrous methanol (30 ml), the compound **15a$_2$** (0.19 mmole) was added. The solution was heated at reflux temperature for 72 hours. The reaction was quenched by adding water (30 ml), followed by extraction with benzene. The products were separated on tlc (Wakogel B10) while eluting with a mixture of diethyl ether-hexane (7:3 v/v) giving **16a** in a 43% yield. b) A mixture of **14a** (0.5 mmole), methyl acetoacetate (3 mmoles) and manganese(III) acetate (4 mmoles) in acetic acid (30 ml) was stirred at 100° for 30 minutes and worked-up in the same way as described previously to give **16a** in a 71% yield.

Compound **16a** was obtained as a colorless microcrystals, mp 207-209° (from methanol-chloroform); ir (chloroform): $\nu = 1687$, 1641 cm^{-1}; ^{1}H nmr (deuteriochloroform): $\delta =$ 1.00-1.10 (4H, br s), 2.13 (6H, s), 3.43 (2H, br s), 3.60 (6H, s), 7.27-7.35 (20H, m); ^{13}C nmr (deuteriochloroform): $\delta =$ 166.1, 166.0, 145.2, 145.0, 141.0, 140.9, 128.0, 127.7, 127.6, 127.0, 126.7, 126.6, 126.1, 126.0, 107.9, 95.2, 50.6, 48.9, 48.2, 29.2, 28.4, 14.7.

Anal. Calcd. for $C_{40}H_{38}O_6$: C, 78.15; H, 6.23. Found: C, 77.63; H, 6.20.

Acknowledgment.

We wish to thank Professor Tsutomu Katsuki of Kyushu University for his discussion and helpful suggestions on the transesterification reaction.

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