

Jie Ouyang

Department of Environmental Science, Graduate School of Science
and Technology, Kumamoto University,
Kurokami 2-39-1, Kumamoto 860, Japan

Hiroshi Nishino and Kazu Kurosawa*

Department of Chemistry,
Faculty of Science, Kumamoto University,
Kurokami 2-39-1, Kumamoto 860, Japan
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The reactions of 1,1-diphenylethene, 1,1-bis(4-chlorophenyl)ethene, 1,1-bis(4-methylphenyl)ethene, and 1,1-bis(4-methoxyphenyl)ethene with 3,5-diacetyl-2,6-heptanedione in the presence of manganese(III) acetate in acetic acid at 80° yielded 4,6-diacetyl-8,8-diaryl-1,3-dimethyl-2,9-dioxabicyclo[4.3.0]non-3-enes (41-48%), 5-acetyl-2,2-diaryl-6-methyl-2,3-dihydrobenzo[*b*]furans (20-21%), 3-acetyl-5,5-diaryl-2-methyl-4,5-dihydrofurans (5-10%), and benzophenones (3-7%). Similarly, the reactions of 1,1-diarylethenes with dimethyl 2,4-diacetyl-1,5-pentanedioate or diethyl 2,4-diacetyl-1,5-pentanedioate gave the corresponding 4,6-bis(alkoxycarbonyl)-8,8-diaryl-1,3-dimethyl-2,9-dioxabicyclo[4.3.0]non-3-enes in moderate yields.

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Introduction.

We and others reported manganic acetate (manganese(III) acetate) or tris(2,4-pentanedionato)manganese(III)-mediated free-radical intermolecular cyclization of alkenes with 1,3-diones [1-4], that gave 3-substituted 5,5-diaryl-2-methyl-4,5-dihydrofurans in good yields. In continuing the study it was found that the photoreaction of 3-acetyl-5,5-diaryl-2-methyl-4,5-dihydrofurans yielded substituted naphthalenes (Scheme 1) [5].

We applied the above manganese(III) acetate-mediated free-radical intermolecular cyclization to the active methylene compounds bearing two reactive sites in the hope to obtain compounds bearing two tetrahydrofuran rings which may have a utility in forming binaphthalenes derivatives by application of the photoreaction. However, the reaction with manganese(III) acetate resulted in the formation of novel heterocyclic compounds that are described in this paper.

Scheme 1

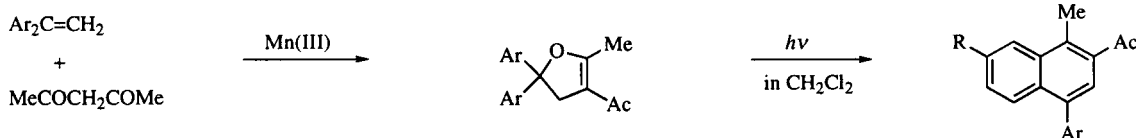


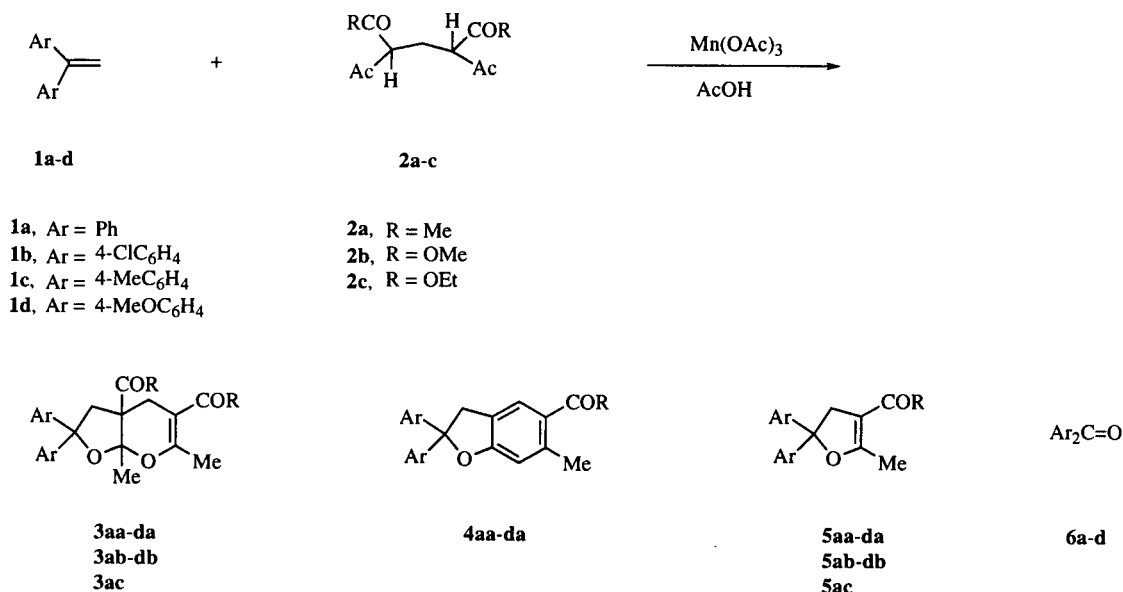
Table 1

Reaction of 1,1-Diphenylethene (**1a**) with 3,5-Diacetyl-2,6-heptanedione (**2a**) in the Presence of Manganese(III) Acetate

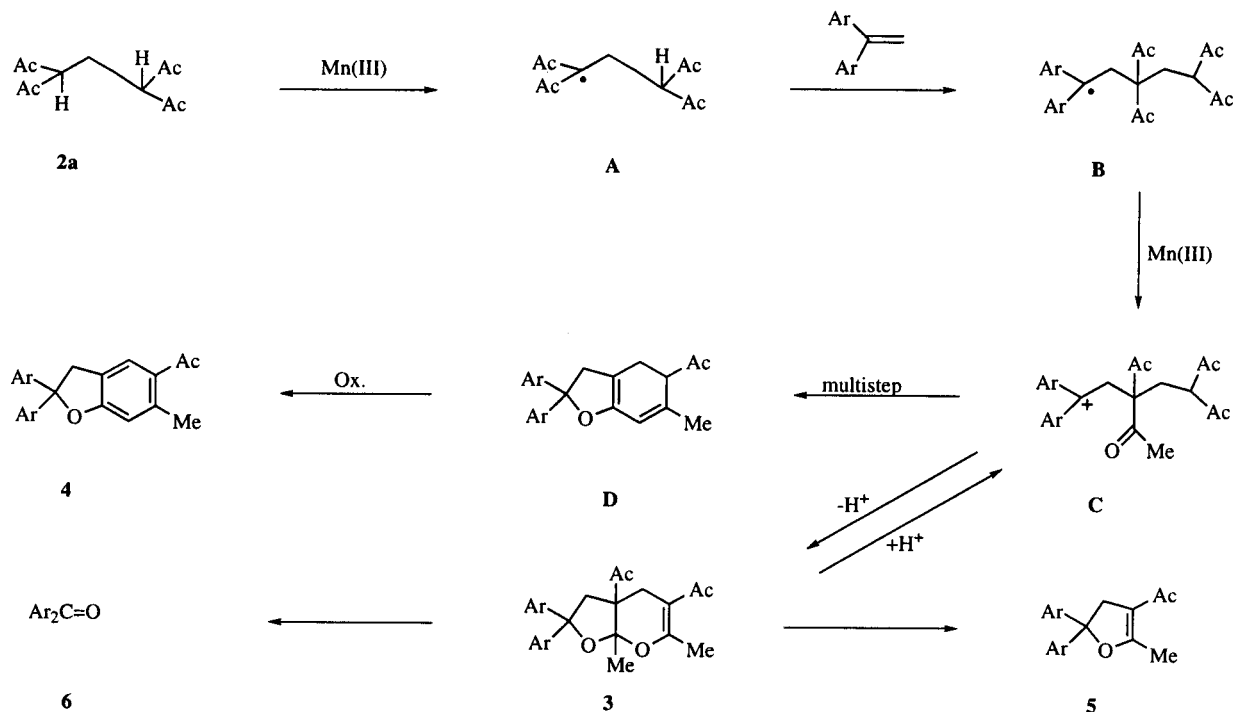
Entry	Molar ratio [a]	Temp °C	Time minutes	Recovery/%					Product (yield/%) [b]				
				1a	3aa	4aa	5aa	6a	1a	3aa	4aa	5aa	6a
1	1:1.5:3.5	100	5	21	24	13	8	3					
2	1:2:6	100	5	3	35	13	9	6					
3	1:2.5:8	100	5		42	17	11	10					
4	1:3:9	70	20		43	15	4	15					
5	1:3:9	80	10		46	21	6	7					
6	1:3:9	100	5		44	23	7	11					
7	1:3:9	120	5		40	22	10	10					
8	1:4:12	100	5		42	15	8	2					

[a] 1,1-Diphenylethene:3,5-diacetyl-2,6-heptanedione:manganese(III) acetate. [b] All the yields are given for chromatographically purified materials based on the alkene used.

Scheme 2



Scheme 3



Results and Discussion.

Reactions of 1,1-Diarylethenes with 3,5-Diacetyl-2,6-heptanedione in the Presence of Manganese(III) Acetate.

When the reaction of 1,1-diphenylethene (**1a**) with 3,5-diacetyl-2,6-heptanedione (**2a**) in the presence of

manganese(III) acetate was carried out by heating in acetic acid at 100° until the dark brown colored solution of manganese(III) acetate turned transparent, the products were found to be 4,6-diacetyl-1,3-dimethyl-8,8-diphenyl-2,9-dioxabicyclo[4.3.0]non-3-ene (**3aa**), 5-acetyl-6-methyl-2,2-diphenyl-2,3-dihydrobenzo[b]furan (**4aa**), 3-ace-

Table 2

Reactions of 1,1-Disubstituted Ethenes **1a-d** with 2,6-Heptanediones **2a-c** in the Presence of Manganese(III) Acetate [a]

Entry	Alkene	2,6-Heptanedione	Product (yield/%) [b]			
5	1a	2a	3aa (46)	4aa (21)	5aa (6)	6a (7)
9	1b	2a	3ba (48)	4ba (22)	5ba (5)	6b (6)
10	1c	2a	3ca (41)	4ca (21)	5ca (10)	6c (3)
11	1d	2a	3da (43)	4da (20)	5da (9)	6d (5)
12	1a	2b	3ab (41)		5ab (4)	6a (5)
13	1b	2b	3bb (30)		5bb (3)	6b (2)
14	1c	2b	3cb (28)		5cb (3)	6c (2)
15	1d	2b	3db (31)		5db (6)	6d (5)
16	1a	2c	3ac (35)		5ac (5)	6a (6)

[a] The reactions are performed at a molar ratio of 1:3:9 for alkene:carbonyl compound:manganese(III) acetate in acetic acid at 80 °C for 10 minutes. [b] All the yields are given for chromatographically purified materials based on the alkene used.

tyl-2-methyl-5,5-diphenyl-4,5-dihydrofuran (**5aa**), and benzophenone (**6a**) (Scheme 2 and Table 1, entry 1).

Yields of **3aa** and **4aa** varied depending on the molar ratio of **1a**:**2a**:manganese(III) acetate. The yields were also depending on the reaction temperature, and the reaction at a lower temperature required longer reaction time (entry 4). The maximum yield for **3aa** was attained when the molar ratio was 1:3:9 at 80° (entry 5). The yields of **4aa** gradually increased with increasing the molar ratio of manganese(III) acetate.

The structures of the products were determined on the basis of ¹H and ¹³C nmr, ir spectra, and elemental analyses. The ¹³C nmr spectrum of **3aa** in deuteriochloroform showed methyl carbon signals at δ 29.9, 27.2, 22.0, and 19.7, methylene carbons at δ 44.8 and 26.9, sp² and sp³ carbons bearing no hydrogen at δ 107.8, 107.7, 86.5, and 59.2, carbonyl carbons at δ 206.7 and 197.7, and eight aromatic and other sp² carbon at δ 162.0, 147.6, 147.1, 128.3, 128.1, 126.6, 126.5, 124.8, and 124.7. The assignments were based on the dept spectrum. Thus, the structure of **3aa** was determined to be 4,6-diacetyl-8,8-diphenyl-1,3-dimethyl-2,9-dioxabicyclo[4.3.0]non-3-ene which is also consistent with the ¹H nmr and ir spectral data. The structure of product **4aa** was similarly determined. Dihydrofuran **5aa** and benzophenone (**6a**) were known compounds and identified on comparison of their ¹H nmr and ir spectra with those of authentic samples.

Then, the generality of the reactions were examined by using 1,1-bis(4-chlorophenyl)ethene (**1b**), 1,1-bis(4-methylphenyl)ethene (**1c**), and 1,1-bis(4-methoxyphenyl)ethene (**1d**) (Table 2). The reactions of **1b-d** with **2a** in the presence of manganese(III) acetate yielded the corresponding dioxabicyclononenes **3ba-3da**, dihydrobenzofurans **4ba-4da**, 3-acetyl-5,5-diaryl-2-methyl-4,5-dihydrofurans **5ba-5da**, and benzophenones **6b-d** (Table 2, entries 9-11). The reactions of dimethyl 2,4-diacetyl-1,5-pentanedioate (**2b**) and diethyl 2,4-diacetyl-1,5-pentanedioate (**2c**) with 1,1-diarylethenes **1a-d** were also examined. Contrary to the reaction of **2a**, the reactions of **2b**

and **2c** did not give 2,3-dihydrobenzo[*b*]furans, but afforded 4,6-bis(alkoxycarbonyl)-8,8-diaryl-1,3-dimethyl-2,9-dioxabicyclo[4.3.0]non-3-enes **3ab-3db** and **3ac** in moderate yields, along with small amounts of alkyl 5,5-diaryl-2-methyl-4,5-dihydrofuran-3-carboxylates **5ab-5db** and **5ac**, and benzophenones **6a-d** (Table 2, entries 12-16).

Reaction Pathways.

The reaction pathways for the formation of dioxabicyclononenes **3** and dihydrobenzofurans **4** could be shown as the following. The reaction of **2a** with manganese(III) acetate gives radicals **A** as has been often observed in a similar reaction of active methylene compounds with manganese(III) acetate [1]. Then, the radicals **A** add to alkene to form radicals **B** which are subsequently oxidized with manganese(III) acetate to the corresponding cation **C**. The cation **C** cyclizes either involving the participation of an acetyl group to form a ketal structure to give **3**, or involving deacetylation, the condensation of the acetyl groups at the 3- and 5-positions, and oxidation to give **4** (Scheme 3). In order to obtain an evidence that the cation **C** is the common intermediate for products **3** and **4**, 4,6-diacetyl-8,8-bis(4-methylphenyl)-1,3-dimethyl-2,9-dioxabicyclo[4.3.0]non-3-ene (**3ca**) was treated with manganese(III) acetate at a molar ratio of 1:3 in acetic acid at 100° for 1 hour. The reaction gave **4ca** (16%), and decomposed products **5ca** (19%) and **6c** (6%) together with many unseparable products. On the other hand, no reaction occurred when **4ca** was treated with manganese(II) acetate. These experiments support that the cation **C** is a possible intermediate both for **3** and **4**. It has been already shown that 1,1-diarylethenes **1a-d** can be directly oxidized to benzophenones for prolonged reaction time [6]. However, the present reaction requires only few minutes, therefore, the benzophenones could be formed from oxidative decomposition of **3** in this reaction.

In conclusion, convenient preparations of 8,8-diaryl-1,3-dimethyl-2,9-dioxabicyclo[4.3.0]non-3-enes and 2,2-diaryl-6-methyl-2,3-dihydrobenzo[*b*]furans are report-

ed. The reactions are easily carried out giving products in moderate yields and should be applicable to the other active methylene compounds.

EXPERIMENTAL

Measurements.

All of the ^1H and ^{13}C nmr spectra were taken with a JNM PMX-60SI (60 MHz) and a JNM EX-90FT nmr (90 MHz for ^1H 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 data are expressed in ν values (cm^{-1}). Mass spectra were taken with a JMS-LX1000 and a Shimadzu QP2000GF mass spectrometer at an ionizing voltage of 70 eV. All of the melting points were determined with a Yanagimoto micromelting-point apparatus MP-J3. Elemental analyses were performed by the Instrumental Analysis Center, Kumamoto University and the Microanalytical Center, Kyushu University, Fukuoka, Japan.

Materials.

Manganese(III) acetate dihydrate was prepared according to the method in the literature [7]. 1,1-Disubstituted ethenes **1a-d** were prepared by dehydration of the corresponding alcohols which were synthesized from substituted acetophenones and arylmagnesium bromides. 3,5-Diacetyl-2,6-heptanedione (**2a**), dimethyl 2,4-diacetyl-1,5-pentanedioate (**2b**), and diethyl 2,4-diacetyl-1,5-pentanedioate (**2c**) were prepared also according to the literature [8].

Reactions of 1,1-Diarylethenes **1a-d** with 3,5-Diacetyl-2,6-heptanedione (**2a**), and Dialkyl 2,4-Diacetyl-1,5-pentanedioates **2b**, **2c** in the Presence of Manganese(III) Acetate in Acetic Acid.

The general procedure for the reaction of 1,1-diarylethenes **1a-d** with 2,6-heptanediones **2a-c** in acetic acid was as follows. A solution of a 1,1-diarylethene (1 mmole) and a 2,6-heptanedione (1.5-4 mmoles) in the presence of manganese(III) acetate in acetic acid (30 ml) was heated at a temperature and for the period of time shown in Tables 1 and 2. The reaction was quenched by adding water (60 ml) and the mixture was then extracted with benzene (3 x 30 ml). After removing the benzene, the resulting products were separated on TLC (Wakogel B10) while eluting with a mixture of hexane-diethyl ether (1:1 v/v). The yields are listed in Tables 1 and 2. The products were further purified for analytical samples by recrystallization from appropriate solvents. Specific details are given below.

Products.

4,6-Diacetyl-1,3-dimethyl-8,8-diphenyl-2,9-dioxabicyclo[4.3.0]non-3-ene (**3aa**).

This compound was obtained as colorless cubes, mp 148-149° (from benzene-hexane); ir (chloroform): $\nu_{\text{max}} = 1700, 1653 \text{ cm}^{-1}$; ^1H nmr (60 MHz, deuteriochloroform): $\delta = 7.50\text{-}7.23$ (10H, m), 3.22 (1H, d, $J = 14 \text{ Hz}$), 2.96 (1H, d, $J = 14 \text{ Hz}$), 2.53 (2H, m), 2.10 (3H, s), 1.93 (3H, s), 1.68 (3H, s), 1.57 (3H, s); ^{13}C nmr (deuteriochloroform): $\delta = 206.7, 197.7, 162.0, 147.6, 147.1, 128.3$ (2C), 128.1 (2C), 126.6, 126.5, 124.8 (2C), 124.7 (2C),

107.8, 107.7, 86.5, 59.2, 44.8, 29.9, 27.2, 26.9, 22.0, 19.7.

Anal. Calcd. for $\text{C}_{25}\text{H}_{26}\text{O}_4$: C, 76.96; H, 6.71. Found: C, 77.11; H, 6.56.

4,6-Diacetyl-8,8-bis(4-chlorophenyl)-1,3-dimethyl-2,9-dioxabicyclo[4.3.0]non-3-ene (**3ba**).

This compound was obtained as colorless cubes, mp 88-90° (from methanol); ir (chloroform): $\nu_{\text{max}} = 1703, 1674 \text{ cm}^{-1}$; ^1H nmr (60 MHz, deuteriochloroform): $\delta = 7.53\text{-}7.17$ (8H, m), 3.18 (1H, d, $J = 14 \text{ Hz}$), 2.87 (1H, d, $J = 14 \text{ Hz}$), 2.57 (2H, s), 2.17 (3H, s), 2.00 (3H, s), 1.77 (3H, s), 1.60 (3H, s); ^{13}C nmr (deuteriochloroform): $\delta = 206.1, 197.6, 161.7, 146.1, 145.1, 132.8, 132.7, 128.6$ (2C), 128.3 (2C), 126.2 (4C), 107.9, 107.7, 85.7, 59.1, 44.6, 30.0, 27.2, 26.9, 21.8, 19.9.

Anal. Calcd. for $\text{C}_{25}\text{H}_{24}\text{Cl}_2\text{O}_4 \cdot 1/2\text{H}_2\text{O}$: C, 64.11; H, 5.38. Found: C, 63.78; H, 5.61.

4,6-Diacetyl-8,8-bis(4-methylphenyl)-1,3-dimethyl-2,9-dioxabicyclo[4.3.0]non-3-ene (**3ca**).

This compound was obtained as colorless cubes, mp 72-74° (from benzene-hexane); ir (chloroform): $\nu_{\text{max}} = 1701, 1671 \text{ cm}^{-1}$; ^1H nmr (60 MHz, deuteriochloroform): $\delta = 7.50\text{-}7.03$ (8H, m), 3.19 (1H, d, $J = 14 \text{ Hz}$), 2.93 (1H, d, $J = 14 \text{ Hz}$), 2.52 (2H, s), 2.65 (6H, s), 2.13 (3H, s), 1.95 (3H, s), 1.72 (3H, s), 1.57 (3H, s); ^{13}C nmr (deuteriochloroform): $\delta = 206.9, 197.8, 162.2, 145.0, 144.5, 136.1, 136.0, 129.0$ (2C), 128.8 (2C), 124.6 (4C), 107.9, 107.8, 86.4, 59.3, 44.7, 29.9, 27.3, 27.0, 22.1, 20.9, 20.8, 19.8.

Anal. Calcd. for $\text{C}_{27}\text{H}_{30}\text{O}_4 \cdot 1/2\text{H}_2\text{O}$: C, 75.85; H, 7.31. Found: C, 76.00; H, 7.58.

4,6-Diacetyl-8,8-bis(4-methoxyphenyl)-1,3-dimethyl-2,9-dioxabicyclo[4.3.0]non-3-ene (**3da**).

This compound was obtained as a colorless liquid; ir (chloroform): $\nu_{\text{max}} = 1700, 1671 \text{ cm}^{-1}$; ^1H nmr (60 MHz, deuteriochloroform): $\delta = 7.50\text{-}6.70$ (8H, m), 3.75 (6H, s), 3.15 (1H, d, $J = 14 \text{ Hz}$), 2.90 (1H, d, $J = 14 \text{ Hz}$), 2.53 (2H, s), 2.13 (3H, s), 1.98 (3H, s), 1.78 (3H, s), 1.58 (3H, s); ^{13}C nmr (deuteriochloroform): $\delta = 206.8, 197.8, 162.2, 158.2$ (2C), 140.3, 139.7, 126.0 (4C), 113.7 (2C), 113.5 (2C), 108.0, 107.8, 86.2, 59.3, 55.2, 55.1, 44.7, 30.0, 27.2, 27.1, 22.1, 20.0.

Anal. Calcd. for $\text{C}_{27}\text{H}_{30}\text{O}_6$: C, 71.98; H, 6.71. Found: C, 71.85; H, 7.13.

4,6-Bis(methoxycarbonyl)-1,3-dimethyl-8,8-diphenyl-2,9-dioxabicyclo[4.3.0]non-3-ene (**3ab**).

This compound was obtained as colorless cubes, mp 117-119° (from methanol); ir (chloroform): $\nu_{\text{max}} = 1725, 1701 \text{ cm}^{-1}$; ^1H nmr (60 MHz, deuteriochloroform): $\delta = 7.55\text{-}7.20$ (10H, m), 3.67 (3H, s), 3.30 (3H, s), 3.29 (1H, d, $J = 14 \text{ Hz}$), 2.85 (1H, d, $J = 14 \text{ Hz}$), 2.70 (2H, s), 1.80 (3H, s), 1.70 (3H, s); ^{13}C nmr (deuteriochloroform): $\delta = 172.7, 168.2, 162.7, 148.1, 146.8, 127.9$ (2C), 127.8 (2C), 126.4, 126.2, 125.2 (2C), 124.9 (2C), 108.5, 96.7, 87.4, 54.2, 51.8, 51.1, 44.5, 27.0, 21.2, 19.2.

Anal. Calcd. for $\text{C}_{25}\text{H}_{26}\text{O}_6 \cdot 3/4\text{H}_2\text{O}$: C, 68.87; H, 6.35. Found: C, 68.82; H, 6.15.

8,8-Bis(4-chlorophenyl)-4,6-bis(methoxycarbonyl)-1,3-dimethyl-2,9-dioxabicyclo[4.3.0]non-3-ene (**3bb**).

This compound was obtained as colorless cubes, mp 147-148° (from methanol); ir (chloroform): $\nu_{\text{max}} = 1730, 1706 \text{ cm}^{-1}$; ^1H nmr (60 MHz, deuteriochloroform): $\delta = 7.53\text{-}7.20$ (8H, m), 3.70

(3H, s), 3.35 (3H, s), 3.24 (1H, d, $J = 14$ Hz), 2.78 (1H, d, $J = 14$ Hz), 2.70 (2H, s), 1.83 (3H, s), 1.70 (3H, s); ^{13}C nmr (deuteriochloroform): $\delta = 172.5, 168.0, 162.3, 146.4, 145.0, 132.5, 132.3, 128.2$ (2C), 128.0 (2C), 126.5 (2C), 126.3 (2C), $108.5, 96.9, 86.6, 54.4, 52.0, 51.2, 44.4, 26.9, 21.1, 19.2$.

Anal. Calcd. for $\text{C}_{25}\text{H}_{24}\text{Cl}_2\text{O}_6$: C, 61.09; H, 4.92. Found: C, 61.03; H, 5.08.

4,6-Bis(methoxycarbonyl)-8,8-bis(4-methylphenyl)-1,3-dimethyl-2,9-dioxabicyclo[4.3.0]non-3-ene (**3cb**).

This compound was obtained as colorless cubes, mp $84-86^\circ$ (from methanol); ir (chloroform): $\nu_{\text{max}} = 1726, 1701\text{ cm}^{-1}$; ^1H nmr (60 MHz, deuteriochloroform): $\delta = 7.43-7.00$ (8H, m), 3.70 (3H, s), 3.31 (3H, s), 3.25 (1H, d, $J = 14$ Hz), 2.82 (1H, d, $J = 14$ Hz), 2.69 (2H, s), 2.25 (6H, s), 1.87 (3H, s), 1.70 (3H, s); ^{13}C nmr (deuteriochloroform): $\delta = 172.8, 168.2, 162.8, 145.2, 144.0, 135.8, 135.6, 128.6$ (2C), 128.4 (2C), 125.1 (2C), 124.9 (2C), $108.5, 96.8, 87.3, 54.2, 51.8, 51.0, 44.4, 27.2, 21.3, 20.9$ (2C), 19.3 .

Anal. Calcd. for $\text{C}_{27}\text{H}_{30}\text{O}_6$: C, 71.98; H, 6.71. Found: C, 71.64; H, 6.85.

4,6-Bis(methoxycarbonyl)-8,8-bis(4-methoxyphenyl)-1,3-dimethyl-2,9-dioxabicyclo[4.3.0]non-3-ene (**3db**).

This compound was obtained as a colorless liquid; ir (chloroform): $\nu_{\text{max}} = 1728, 1703\text{ cm}^{-1}$; ^1H nmr (60 MHz, deuteriochloroform): $\delta = 7.40-6.70$ (8H, m), 3.73 (6H, s), 3.67 (3H, s), 3.30 (3H, s), 3.20 (1H, d, $J = 14$ Hz), 2.79 (1H, d, $J = 14$ Hz), 2.67 (2H, s), 1.90 (3H, s), 1.70 (3H, s); ^{13}C nmr (deuteriochloroform): $\delta = 172.9, 168.3, 162.8, 158.1, 158.0, 140.4, 139.2, 126.5$ (2C), 126.3 (2C), 113.3 (2C), 113.1 (2C), $108.6, 96.8, 87.1, 55.2$ (2C), $54.3, 51.9, 51.1, 44.5, 27.2, 21.3, 19.4$.

Anal. Calcd. for $\text{C}_{27}\text{H}_{30}\text{O}_8$: C, 67.20; H, 6.27. Found: C, 67.18; H, 6.57.

4,6-Bis(ethoxycarbonyl)-1,3-dimethyl-8,8-diphenyl-2,9-dioxabicyclo[4.3.0]non-3-ene (**3ac**).

This compound was obtained as colorless cubes, mp $92-94^\circ$ (from benzene-hexane); ir (chloroform): $\nu_{\text{max}} = 1719, 1700\text{ cm}^{-1}$; ^1H nmr (60 MHz, deuteriochloroform): $\delta = 7.50-7.13$ (10H, m), 4.13 (2H, q, $J = 7$ Hz), 3.80 (2H, q, $J = 7$ Hz), 3.32 (1H, d, $J = 14$ Hz), 2.86 (1H, d, $J = 14$ Hz), 2.73 (2H, s), 1.77 (3H, s), 1.73 (3H, s), 1.23 (3H, t, $J = 7$ Hz), 0.80 (3H, t, $J = 7$ Hz); ^{13}C nmr (deuteriochloroform): $\delta = 172.4, 167.9, 162.5, 148.4, 147.1, 127.9$ (2C), 127.8 (2C), $126.3, 126.2, 125.1$ (2C), 124.9 (2C), $108.5, 97.0, 87.4, 61.1, 59.8, 54.4, 44.4, 27.1, 21.3, 19.1, 14.4, 13.3$.

Anal. Calcd. for $\text{C}_{27}\text{H}_{30}\text{O}_6$: C, 71.98; H, 6.71. Found: C, 72.17; H, 6.84.

5-Acetyl-6-methyl-2,2-diphenyl-2,3-dihydrobenzo[b]furan (**4aa**).

This compound was obtained as colorless cubes, mp $139-140^\circ$ (from benzene-hexane); ir (chloroform): $\nu_{\text{max}} = 1670\text{ cm}^{-1}$; ^1H nmr (60 MHz, deuteriochloroform): $\delta = 7.60$ (1H, s), $7.53-7.23$ (10H, m), 6.83 (1H, s), 3.90 (2H, s), 2.55 (3H, s), 2.50 (3H, s); ^{13}C nmr (deuteriochloroform): $\delta = 199.4, 161.4, 144.8$ (2C), $142.0, 130.7, 128.4$ (4C), 127.6 (2C), $127.1, 125.9$ (4C), $123.8, 113.0, 93.9, 43.7, 29.3, 22.8$; ms: m/z (relative intensity) = 328 (74, M^+), 313 (100), 178 (13), 165 (20), 91 (13), 77 (16), 51 (13), 43 (69).

Anal. Calcd. for $\text{C}_{23}\text{H}_{20}\text{O}_2$: C, 84.12; H, 6.14. Found: C, 84.28; H, 6.16.

5-Acetyl-2,2-bis(4-chlorophenyl)-6-methyl-2,3-dihydrobenzo[b]furan (**4ba**).

This compound was obtained as a colorless liquid; ir (chloroform): $\nu_{\text{max}} = 1671\text{ cm}^{-1}$; ^1H nmr (60 MHz, deuteriochloroform): $\delta = 7.67$ (1H, s), $7.40-7.33$ (8H, m), 6.85 (1H, s), 3.85 (2H, s), 2.53 (3H, s), 2.50 (3H, s); ^{13}C nmr (deuteriochloroform): $\delta = 199.4, 160.9, 142.8$ (2C), $142.1, 133.9$ (2C), $131.0, 128.7$ (4C), 127.3 (4C), $127.1, 123.2, 113.1, 92.9, 43.6, 29.3, 22.7$; ms: m/z (relative intensity) = 396 (51, M^+), 398 (35), 382 (21), 381 (88), 125 (10), 93 (10), 43 (100).

Anal. Calcd. for $\text{C}_{23}\text{H}_{18}\text{Cl}_2\text{O}_2 \cdot 1/2\text{H}_2\text{O}$: C, 67.99; H, 4.71. Found: C, 67.71; H, 4.75.

5-Acetyl-2,2-bis(4-methylphenyl)-6-methyl-2,3-dihydrobenzo[b]furan (**4ca**).

This compound was obtained as a colorless liquid; ir (chloroform): $\nu_{\text{max}} = 1669\text{ cm}^{-1}$; ^1H nmr (60 MHz, deuteriochloroform): $\delta = 7.67$ (1H, s), $7.50-7.10$ (8H, m), 6.85 (1H, s), 3.90 (2H, s), 2.57 (3H, s), 2.50 (3H, s), 2.30 (6H, s); ^{13}C nmr (deuteriochloroform): $\delta = 199.3, 161.5, 142.0$ (2C), $141.9, 137.2$ (2C), $130.4, 129.0$ (4C), $127.2, 125.8$ (4C), $124.0, 113.0, 94.0, 43.6, 29.2, 22.8, 21.0$ (2C); ms: m/z (relative intensity) = 356 (96, M^+), 341 (100), 221 (13), 178 (23), 105 (11), 91 (12), 65 (11), 43 (83).

Anal. Calcd. for $\text{C}_{25}\text{H}_{24}\text{O}_2$: C, 84.24; H, 6.79. Found: C, 84.13; H, 7.00.

5-Acetyl-2,2-bis(4-methoxyphenyl)-6-methyl-2,3-dihydrobenzo[b]furan (**4da**).

This compound was obtained as a colorless liquid; ir (chloroform): $\nu_{\text{max}} = 1667\text{ cm}^{-1}$; ^1H nmr (60 MHz, deuteriochloroform): $\delta = 7.58$ (1H, s), $7.40-6.74$ (8H, m), 6.73 (1H, s), 3.83 (2H, s), 3.73 (6H, s), 2.53 (3H, s), 2.43 (3H, s); ^{13}C nmr (deuteriochloroform): $\delta = 199.4, 161.5, 159.0$ (2C), $142.0, 137.1$ (2C), $130.5, 127.3$ (4C), $127.2, 124.0, 113.7$ (4C), $113.0, 93.8, 55.3$ (2C), $43.8, 29.2, 22.8$; ms: m/z (relative intensity) = 388 (4, M^+), 372 (100), 356 (20), 342 (10), 263 (27), 232 (11), 220 (20), 208 (48), 121 (31), 108 (22).

Anal. Calcd. for $\text{C}_{25}\text{H}_{24}\text{O}_4$: C, 77.30; H, 6.23. Found: C, 77.22; H, 6.45.

3-Acetyl-2-methyl-5,5-diphenyl-4,5-dihydrofuran (**5aa**).

This compound was obtained as a colorless liquid, bp $180-185^\circ/1\text{ mm Hg}$ (bath temperature) [2].

3-Acetyl-5,5-bis(4-chlorophenyl)-2-methyl-4,5-dihydrofuran (**5ba**).

This compound was obtained as colorless cubes, mp $95-96^\circ$ (from petroleum ether, bp $30-70^\circ$) (lit $95-96^\circ$) [3b].

3-Acetyl-5,5-bis(4-methylphenyl)-2-methyl-4,5-dihydrofuran (**5ca**).

This compound was obtained as a pale yellow liquid [3b].

3-Acetyl-5,5-bis(4-methoxyphenyl)-2-methyl-4,5-dihydrofuran (**5da**).

This compound was obtained as colorless needles, mp $96-97^\circ$ (from benzene-petroleum ether, bp $30-70^\circ$) (lit $96-96.5^\circ$) [2].

Methyl 2-Methyl-5,5-diphenyl-4,5-dihydrofuran-3-carboxylate (5ab).

This compound was obtained as a colorless liquid; ir (chloroform): $\nu_{\max}$ = 1687, 1649 cm^{-1} ; ^1H nmr (60 MHz, deuteriochloroform): δ = 7.50-7.25 (10H, m), 3.70 (3H, s), 3.65 (2H, q, J = 1.6 Hz), 2.33 (3H, t, J = 1.6 Hz); ^{13}C nmr (deuteriochloroform): δ = 166.4, 165.9, 145.0 (2C), 128.2 (4C), 127.4 (2C), 125.5 (4C), 101.4, 91.5, 50.6, 43.9, 14.0; ms: m/z (relative intensity) = 294 (4, M^+), 263 (9), 262 (28), 252 (26), 247 (26), 192 (17), 191 (55), 165 (16), 77 (10), 43 (100).

Anal. Calcd. for $\text{C}_{19}\text{H}_{18}\text{O}_3$: M, 294.1256. Found: m/z = 294.1250.

Methyl 5,5-Bis(4-chlorophenyl)-2-methyl-4,5-dihydrofuran-3-carboxylate (5bb).

This compound had mp 108-110° (from hexane); ir (chloroform): $\nu_{\max}$ = 1691, 1652 cm^{-1} ; ^1H nmr (60 MHz, deuteriochloroform): δ = 7.30 (8H, s), 3.70 (3H, s), 3.53 (2H, q, J = 1.6 Hz), 2.30 (3H, t, J = 1.6 Hz); ^{13}C nmr (deuteriochloroform): δ = 166.1, 165.7, 143.1 (2C), 133.6 (2C), 128.5 (4C), 125.5 (4C), 101.5, 90.5, 50.8, 43.9, 14.0; ms: m/z (relative intensity) = 362 (1, M^+), 332 (5.4), 330 (8), 320 (7), 259 (7), 225 (6), 189 (9), 111 (2), 43 (100).

Anal. Calcd. for $\text{C}_{19}\text{H}_{16}\text{Cl}_2\text{O}_3$: C, 62.83; H, 4.44. Found: C, 62.89; H, 4.40.

Methyl 5,5-Bis(4-methylphenyl)-2-methyl-4,5-dihydrofuran-3-carboxylate (5cb).

This compound was obtained as a colorless liquid; ir (chloroform): $\nu_{\max}$ = 1686, 1646 cm^{-1} ; ^1H nmr (60 MHz, deuteriochloroform): δ = 7.33-7.00 (8H, s), 3.63 (3H, s), 3.55 (2H, q, J = 1.6 Hz), 2.27 (9H, br s); ^{13}C nmr (deuteriochloroform): δ = 166.4, 165.9, 142.2 (2C), 136.9 (2C), 128.8 (4C), 125.4 (4C), 101.3, 91.5, 50.5, 43.9, 20.7 (2C), 14.0; ms: m/z (relative intensity) = 322 (2, M^+), 290 (29), 280 (47), 275 (24), 205 (15), 178 (13), 91 (10), 43 (100).

Anal. Calcd. for $\text{C}_{21}\text{H}_{22}\text{O}_3$: C, 78.23; H, 6.88. Found: C, 78.15; H, 7.05.

Methyl 5,5-Bis(4-methoxyphenyl)-2-methyl-4,5-dihydrofuran-3-carboxylate (5db).

This compound was obtained as a colorless liquid; ir (chloro-

form): $\nu_{\max}$ = 1686, 1645 cm^{-1} ; ^1H nmr (60 MHz, deuteriochloroform): δ = 7.40-6.80 (8H, m), 3.73 (6H, s), 3.69 (3H, s), 3.55 (2H, q, J = 1.6 Hz), 2.31 (3H, t, J = 1.6 Hz); ^{13}C nmr (deuteriochloroform): δ = 166.6, 166.2, 158.9 (2C), 137.4 (2C), 127.0 (4C), 113.5 (4C), 101.3, 91.4, 55.2 (2C), 50.7, 44.1, 14.2; ms: m/z (relative intensity) = 354 (3, M^+), 322 (25), 312 (60), 251 (86), 208 (14), 165 (15), 43 (100).

Anal. Calcd. for $\text{C}_{21}\text{H}_{22}\text{O}_5$: C, 71.17; H, 6.16. Found: C, 71.69; H, 6.49.

Ethyl 2-Methyl-5,5-diphenyl-4,5-dihydrofuran-3-carboxylate (5ac).

This compound was obtained as a colorless liquid [6].

Treatment of 4,6-Diacetyl-8,8-bis(4-methylphenyl)-1,3-dimethyl-2,9-dioxabicyclo[4.3.0]non-3-ene (3ca) with Manganese(III) Acetate in Acetic Acid.

A mixture of 3ca (192 mg) and manganese(III) acetate dihydrate (341 mg) in acetic acid (30 ml) was heated at 100° for 1 hour. The reaction mixture was separated in a manner similar to those of the reactions of 1 and 2 in the presence of manganese(III) acetate to give 3ca (36 mg, 14%), 4ca (23 mg, 16%), 5ca (23 mg, 19%), and 6c (5 mg, 6%), being identified with authentic samples.

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