Manganese(III)-Mediated Oxidative Radical Cyclization 2.[1] Reaction of 1,1,ω,ω-Tetraarylsubstituted Terminal Alkadienes with Malonamide or Acetoacetamide

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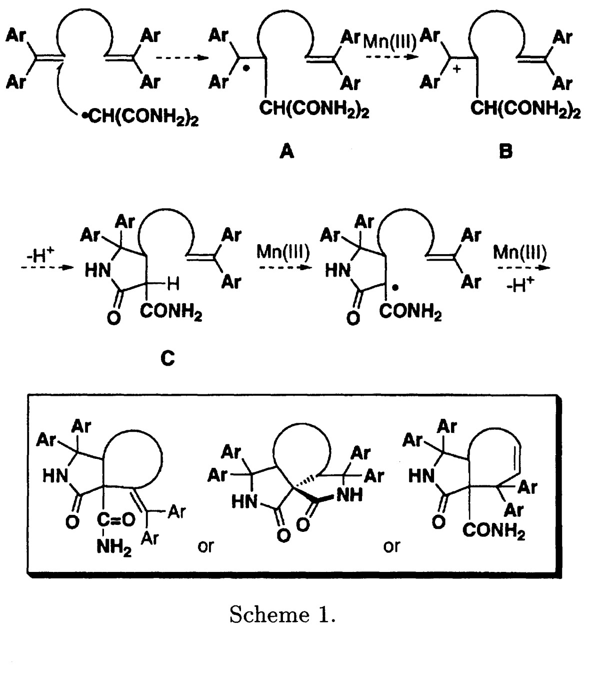
The oxidation of 1,1,6,6-tetraaryl-1,5-hexadienes with manganese(III) acetate in the presence of malonamide gave two types of 5-exo cyclization products, 1-carbamoyl-8-diarylmethylene-3-azabicyclo[3.3.0]octan-2-ones and 3,10-dioxatricyclo[6.3.0.0^{1,5}]undecane-2,11-diones, in good to moderate yields. Similar reactions of 1,1,5,5-tetraaryl-1,4-pentadienes or 1,1,7,7-tetraaryl-1,6-heptadienes with malonamide yielded only complex mixtures, except for the formation of a small amount of 3,11-dioxatricyclo[7.3.0.0^{1,5}]dodecane-2,12-dione. On the other hand, 1,1,5,5-tetraaryl-1,4-pentadienes reacted with acetoacetamide in the presence of manganese(III) acetate to afford 3-carbamoyl-2-methyl-4-(2-propenyl)-4,5-dihydrofurans and 1,4-pentadienes substituted at the 3-position with acetoacetamide. A similar reaction of 1,1,6,6-tetraaryl-1,5-hexadienes with acetoacetamide gave 8-[acetoxy(diaryl)methyl]-3-oxabicyclo[3.3.0]octan-2-one, 1-acetyl-8-diarylmethylene-3-azabicyclo[3.3.0]-octan-2-ones, and 4-(3-butenyl)-3-carbamoyl-2-methyl-4,5-dihydrofurans. The selectivity of the inter- and intramolecular cyclizations containing the carboxamide moiety of malonamide or acetoacetamide is discussed.

Carbon–carbon bond formations using metal-induced free-radical reactions have recently been advanced. Especially, one-pot syntheses using intramolecular tandem and triple free-radical cyclization have been developed,[2] because these radical cyclizations can be applied to the synthesis of natural-product frameworks.[3] In this context, manganese(III)-mediated free-radical cyclizations have something attractive in terms of successive C–C bond formations.[4—9] We have been interested in the synthetic approach for inter- and intramolecular free-radical cyclization using the manganese(III) oxidation of alkenes;[1,4,5,10] we[11a,11b] and another group[11c,11d] have reported a unique spirolactone synthesis. Malonic acid is very easily oxidized with manganese(III) acetate to give the malonic acid radical, ·CH(CO$_2$H)$_2$, which reacts with an alkene to yield a spirodi-γ-lactone in good yield. Malonamide is also oxidized with manganese(III) acetate, giving the corresponding bis(carbamoyl)methyl radical, ·CH(CONH$_2$)$_2$, which reacts with alkenes to yield lactams.[12] In this reaction, the use of 1,ω-dienes gave us the synthetic potential for azapolycyclic compounds. We paid particular attention to 1,1,6,6-tetraaryl-1,5-hexadienes for the following reasons: 1. The 1,3-dicarbonyl radicals specifically attack the C-2 position of the dienes (Scheme 1). The resulting tertiary radicals **A** are readily oxidized with manganese(III) complexes to give tertiary cations **B**, which would be stabilized by the geminal diaryl groups.[13] Therefore, the first cyclization would be easily accomplished to yield monocyclized compounds **C**. 2. Subsequent oxidation of **C** with the manganese(III) complex would occur, since the intermediate **C** has a methine proton which would be easily oxidized, and 5-*exo* and/or 6-*endo* intramolecular radical cyclizations could be achieved. Furthermore, we have been interested in whether oxidative cyclization occurs on the softer nitrogen or the harder oxygen atom

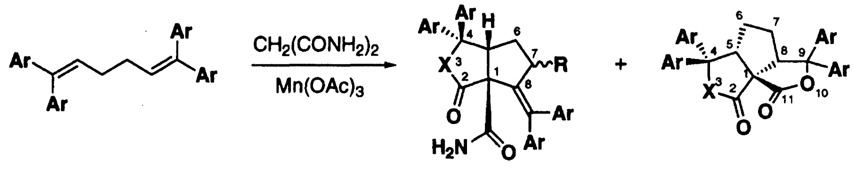


Scheme 1.

of the carboxamide moiety.[12] Intermediate cations **B** of 1,1,ω,ω-tetraarylsubstituted terminal dienes, having electron-donating groups on the aromatic ring, should be softer; we thus hoped that cyclization would occur on the nitrogen atom to give *N*-cyclized products.[12] Accordingly, we focused in the present study on the reaction of 1,1,ω,ω-tetraarylsubstituted terminal dienes with malonamide or acetoacetamide using manganese(III) acetate.

Results and Discussion

Reaction of 1,1,ω,ω-Tetraarylsubstituted Terminal Alkadienes with Malonamide. When a mixture of 1,1,6,6-tetraphenyl-1,5-hexadiene (**1a**) and malonamide was oxidized with manganese(III) acetate under various reaction conditions, two major products (**2a** and **5a**) and two minor products (**3a** and **4a**) were obtained (Scheme 2 and Table 1, Entries 1—4). The structures of **2a** and **5a** were determined to be 1-carbamoyl-8-(diphenylmethylene)-4,4-diphenyl-3-azabicyclo[3.3.0]octan-2-one and 4,4,9,9-tetraphenyl-3,10-dioxatricyclo[6.3.0.0^{1,5}]undecane-2,11-dione,[11c] respectively, based on their spectral data and elemental analyses. The stereochemistry of **2a** was particularly intriguing to us because some thermodynamically less favorable *trans* fused bicyclo[3.3.0]octanes were known,[14] and Snider et al. obtained a small amount of *trans* fused bicyclo[3.3.0]octane by the oxidation of methyl 2-(3-methyl-2-butenyl)-3-oxo-6-heptenoate with manganese(III) acetate.[5a] In order to establish the stereochemistry of **2a**, we performed an NOE experiment between a proton on the ring junction and the carbamoyl group. However, the NOE enhancement was not clear, and there was no method to corroborate the stereochemistry, except for X-ray single-crystal analysis. Therefore, we grew a single crystal of pure **2a** from chloroform–ethanol in the triclinic space group $P\bar{1}$ with a=9.205(3), b=12.481(3), c=12.811(4) Å, α=72.48(2)°, β=88.91(2)°, and γ=69.02(2)°. The crystal structure was solved by direct methods (see full details in the Experimental), and **2a** was found to be the *cis* fused bicyclo[3.3.0]octane shown in Fig. 1.[15] Additionally, the diagram of the unit cell in Fig. 2 shows a 1 : 1 mixture of optical isomers at the C-1 and C-5 positions.



1a-e
a : Ar=Ph
b : Ar=4-FC$_6$H$_4$
c : Ar=4-ClC$_6$H$_4$
d : Ar=4-MeC$_6$H$_4$
e : Ar=4-MeOC$_6$H$_4$

2a-e : R=H, X=NH
3a-c : R=OAc, X=NH
4a-e : R=H, X=O

5a-d : X=O
6d : X=NH

Scheme 2.

Table 1. Reaction of 1,5-Hexadienes **1a**—**e** with Malonamide in the Presence of Manganese(III) Acetate[a]

Entry	1,5-Hexadiene	Molar ratio[b]	Reaction time/min	Product (yield/%)[c]					Recovery of **1**/%
1	**1a**	1 : 4 : 4	1	**2a** (44)		**4a** (3)	**5a** (37)		6
2	**1a**	1 : 4 : 5	1	**2a** (55)	**3a** (3)	**4a** (2)	**5a** (37)		
3	**1a**	1 : 4 : 7	12	**2a** (44)	**3a** (14)	**4a** (2)	**5a** (33)		
4	**1a**	1 : 4 : 8	18	**2a** (31)	**3a** (24)		**5a** (16)		
5[d]	**1a**	1 : 4 : 4	24 h	**2a** (54)			**5a** (12)		7
6[e]	**1a**	1 : 4 : 4	24 h	**2a** (53)			**5a** (12)		9
7	**1b**	1 : 4 : 4	2	**2b** (36)		**4b** (10)	**5b** (38)		10
8	**1b**	1 : 4 : 5	12	**2b** (33)	**3b** (10)	**4b** (9)	**5b** (33)		
9	**1c**	1 : 4 : 6	2	**2c** (42)	**3c** (6)	**4c** (6)	**5c** (36)		
10	**1c**	1 : 4 : 7	5	**2c** (35)	**3c** (10)	**4c** (5)	**5c** (38)		
11	**1d**	1 : 4 : 5	1	**2d** (63)		**4d** (7)	**5d** (13)	**6d** (8)	
12[f]	**1e**	1 : 4 : 5	3	**2e** (72)		**4e** (8)			

a) The reaction was carried out in acetic acid (30 mL) at reflux temperature. b) 1,5-Hexadiene (0.5 mmol) : malonamide : manganese(III) acetate. c) Isolated yield based on the amount of the hexadiene used. d) The reaction was conducted under argon at 23 °C. e) The reaction was done under argon at 23 °C in the presence of Cu(OAc)$_2$ (1.0 mmol) as a co-oxidant. f) The reaction was carried out at 95 °C.

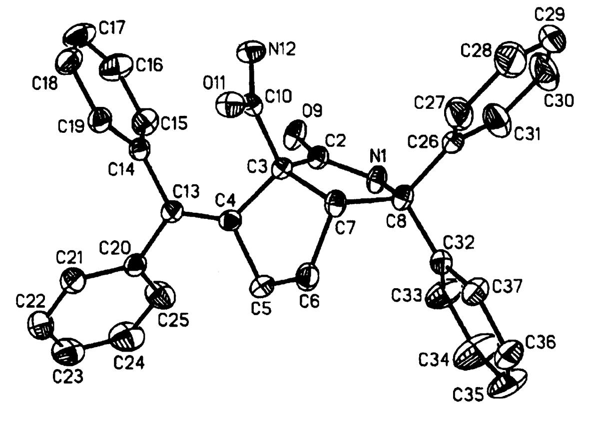


Fig. 1. ORTEP diagram of **2a**. The thermal ellipsoids are 30% equiprobability envelopes, with hydrogens omitted for clarity.

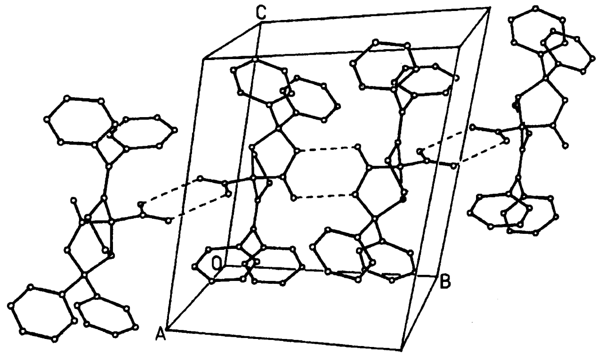


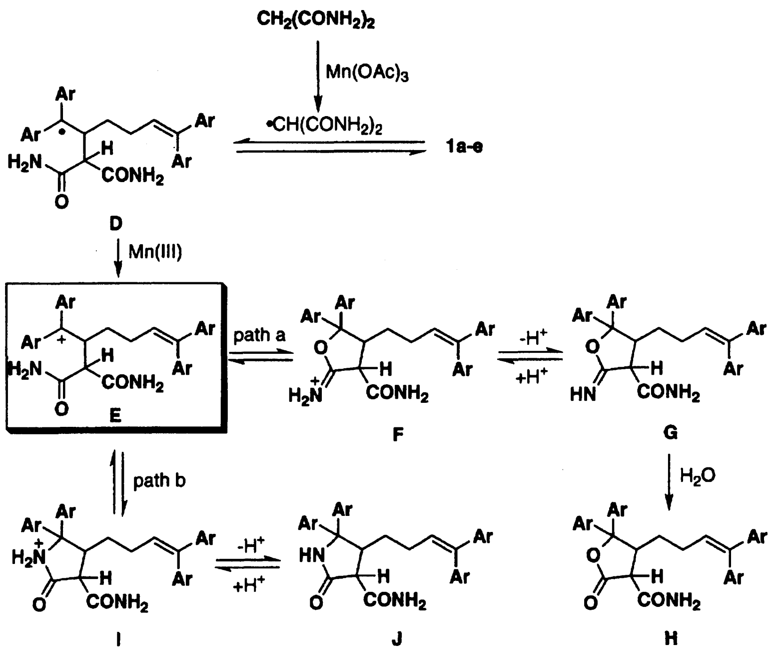
Fig. 2. Packing diagram of **2a** in the unit cell, as viewed into the *a* axis. Both types of intermolecular hydrogen bonds are shown, indicated by dashed lines.

The ^{13}C NMR spectrum of **3a** was very similar to that of **2a**, except that an acetyl and an *O*-methine group newly appeared and one of the methylene groups disappeared (see Experimental). In addition, all of the peaks appeared double and the ^{1}H NMR spectrum showed two acetoxyl groups (1.5 H respectively), which indicates a 1 : 1 stereoisomeric mixture.[16] Consequently, the structure of **3a** was determined to be a derivative of **2a** having an acetoxyl group at C-7. The other minor product **4a** was a bicyclic γ-lactone, 1-carbamoyl-8-diphenylmethylene-4,4-diphenyl-3-oxabicyclo[3.3.0]octan-2-one. The use of more than a stoichiometric amount of manganese(III) acetate led to a decrease in **2a** and an increase in **3a** (Entries 3 and 4). In order to elucidate the formation of **3a**, the oxidation of **2a** with manganese(III) acetate was examined because allylic oxidation of **2a** might yield **3a**. The oxidation was carried out in boiling acetic acid for 8 h. However, no acetoxyl derivatives were detected, and unchanged **2a** was recovered. This means that the acetoxyl group is not introduced after producing **2a**, but, rather, during the reaction. The 3,10-dioxatricyclo[6.3.0.0^{1,5}]undecane-2,11-dione **5a** was also reported by Fristad and Hershberger in the manganese(III)-mediated spirodilactonization of **1a** with malonic acid; they could obtain **5a** only in 12% yield.[11c] However, in our reaction system **5a** was isolated in 37% maximum yield.

Although diaza compounds, such as tricyclic bislactams and 6-*endo* cyclization products, were unfortunately not formed, 5-*exo* azacyclization products were certainly produced, as expected. Similar reactions of 1,1,6,6-tetrakis(4-fluorophenyl)- (**1b**) and 1,1,6,6-tetrakis(4-chlorophenyl)-1,5-hexadiene (**1c**) gave **2b**, **2c**, and **5b**, **5c** along with small amounts of acetates **3b**, **3c** and bicyclolactones **4b**, **4c** (Entries 7—10). When the reactions of electron-rich 1,1,6,6-tetrasubstituted 1,5-hexadienes **1d** and **1e** were conducted under similar reaction conditions, *N*-cyclized 5-*exo* products **2d** and **2e** were mainly produced (Entries 11 and 12). In the case of the reaction of **1d**, a small amount of tricyclic compound **6d**, which has a 3-aza-10-oxatricyclo[6.3.0.0^{1,5}]undecane-2,11-dione skeleton, was also obtained. The yields are summarized in Table 1.

In the reaction of **1a** at 23 °C under argon,[17] overoxidation was inhibited and **2a** was mainly produced, though the reaction required quite a long reaction time (Entry 5). Recently, the use of copper(II) acetate as a co-oxidant in manganese(III) oxidations has been developed to insure oxidative termination.[5a] Primary and secondary radicals react with copper(II) acetate to form organocopper intermediates, which undergo a β-hydride elimination or ligand-transfer oxidation to give alkenes or ligand substituted alkanes.[5a,18] Tertiary and benzyl radicals are easily oxidized by copper(II) acetate at ambient temperature to give the corresponding cations.[18] However, the addition of copper(II) acetate to the present reaction had no effect on the product distribution (Entry 6).

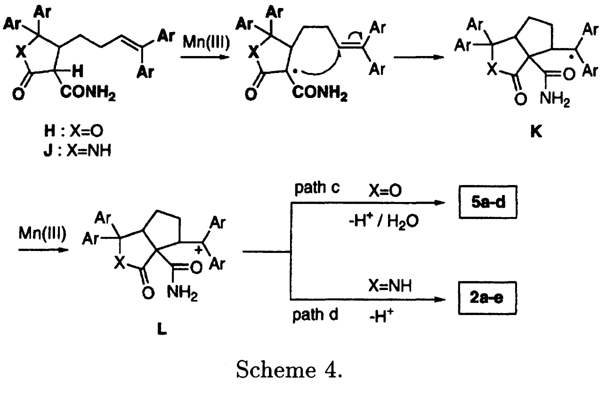
A priori, it was not clear why cyclization occurs via the nitrogen or oxygen atom of the carboxamide moiety in the initial cations **E** (Scheme 3).[12,19] As shown in Table 1, 1,1,6,6-tetrasubstituted 1,5-hexadienes having 4-methylphenyl (**1d**), or 4-methoxyphenyl groups (**1e**) predominantly gave azabicyclic compounds (**2d** and **2e**) (Entries 11 and 12). However, in the cases of dienes having phenyl (**1a**), 4-fluorophenyl (**1b**), and 4-chlorophenyl (**1c**) groups, similar amounts of aza (**2a**, **b**, **c**) and oxacyclic compounds (**5a**, **b**, **c**) were obtained (Entries 2, 7, 9). These results support the idea that electron donation on the geminal aryl groups precedes path b. That is to say, the initial cations **E** would cyclize on the nitrogen atom, which is softer than an oxygen atom, since the cation **E** becomes a softer cation due to electron-donating groups on the aryl groups.[20] Intermediates **H** and **J** would be oxidized in a similar manner, and followed to cyclize intramolecularly to give 5-*exo* cyclized tertiary radicals **K**, which should be energetically favored structures.[5a] After subsequent oxidation of the tertiary radicals **K**, a third cyclization would mainly occur on the oxygen atom of the carboxamide moiety when X=O in the cation **L** (path c in Scheme 4); the corresponding



Scheme 3.

tricyclic compounds **5a**—**d** were obtained after hydrolysis. On the other hand, in the case of X=NH in the cation **L**, β-proton elimination might readily occur; the corresponding azabicyclic compounds **2a**—**e** were preferentially formed (path d). It was therefore considered that the selectivity of paths c and d did not depend on the hard and soft character of the cation **L**, but on the structural strain of the final products. That is, because, in general, ether oxygen bonds of a γ-lactone are more flexible than secondary amino bonds of a γ-lactam, 3,10-dioxatricycloundecanes would be formed, as expected. In contrast, more strained 3,10-diazatricycloundecanes could not be produced and the β-proton elimination from the cation **L** could preferentially occur, which would give less-strained azabicyclooctanes.

In order to apply this reaction to other 1,ω-alkadienes, 1,1,5,5-tetrasubstituted 1,4-pentadienes and 1,1,7,7-tetrasubstituted 1,6-heptadienes were examined. However, the reactions were very complicated, and no polycyclic compounds were isolated, except for the reaction of 1,1,7,7-tetrakis(4-chlorophenyl)-1,6-heptadiene, giving 4,4,10,10-tetrakis(4-chlorophenyl)-3,11-dioxatricyclo[7.3.0.0^{1,5}]dodecane-2,12-dione (11% yield) as the only isolable product (Fig. 3).



Scheme 4.

Reaction of 1,1,ω,ω-Tetraarylsubstituted Terminal Alkadienes with Acetoacetamide. A plan to clarify the mode of cyclization at the nitrogen atom or the oxygen atom prompted us to explore similar reactions using acetoacetamide instead of malonamide. In addition, we also hoped to elucidate which group is most efficient for cyclization, the acetyl or the carboxamide moiety of acetoacetamide. The 1,5-hexadienes **1a**, **1c**, and **1d** reacted with acetoacetamide under similar conditions to afford 1-acetyl-3-azabicyclo[3.3.0]octan-2-ones **7a**, **7c**, **7d**, 8-[acetoxy(diaryl)methyl]-3-oxabicyclo[3.3.0]octan-2-ones **8a**, **8c**, and 3-carbamoyl-4-(4,4-diaryl-3-butenyl)-2-methyl-4,5-dihydrofurans **9a**, **9c**, **9d** as isolable products (Scheme 5 and Table 2). If the cyclization occurs at the carboxamide moiety of acetoacetamide, bicyclolactams **7a**, **c**, **d** and bicyclolactones **8a**, **c** should be formed. On the other hand, if the cyclization proceeds at the acetyl oxygen of acetoacetamide, dihydrofurans **9a**, **c**, **d** must be obtained.[1] The corresponding tricyclo[6.3.0.0^{1,5}]undecane would not be formed for stability and mechanistic reasons. According to the product distribution in Table 2, no difference in the facility of cyclization on the carboxamide or acetyl moiety was recognized. However, the reactivity of the nitrogen and oxygen atoms in the carboxamide

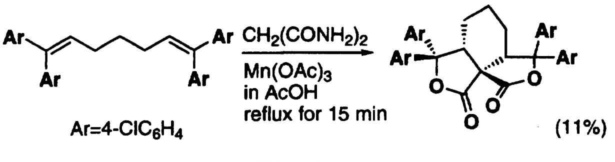
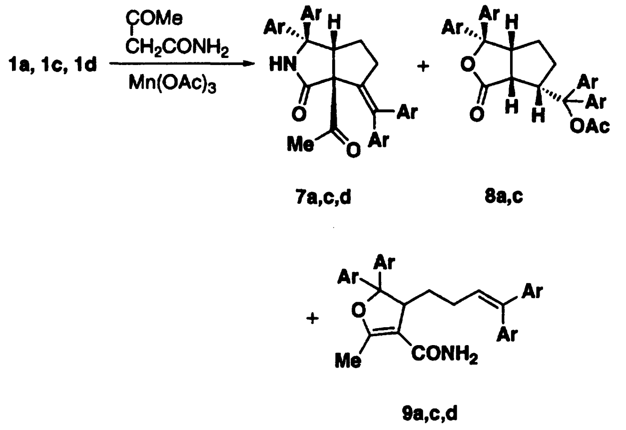


Fig. 3.

Table 2. Reaction of 1,5-Hexadienes **1a**, **1c**, and **1d** with Acetoacetamide in the Presence of Manganese(III) Acetate[a)]

Entry	1,5-Hexadiene	Molar ratio[b)]	Conversion of 1,5-hexadiene/%	Product (yield/%)[c)]		
13	**1a**	3 : 1 : 4	84[d)]	**7a** (29)[e)]	**8a** (11)[e)]	**9a** (36)[e)]
14	**1a**	1 : 2 : 5	81	**7a** (22)	**8a** (5)	**9a** (24)
15	**1c**	1 : 2 : 5	82	**7c** (16)	**8c** (6)	**9c** (23)
16	**1d**	1 : 4 : 4	91	**7d** (19)		**9d** (16)
17	**1d**	1 : 4 : 6	100	**7d** (26)		**9d** (7)

a) The reaction was carried out in boiling acetic acid (30 mL) for 1 min. b) 1,5-Hexadiene (0.5 mmol) : acetoacetamide : manganese(III) acetate. c) Isolated yield based on the hexadiene added. d) The conversion based on the acetoacetamide added. e) Isolated yield based on the acetoacetamide added.



Scheme 5.

moiety revealed a remarkable difference. That is, *N*-cyclized compounds **7a**, **c**, **d** were preferentially produced regardless of the substituent effect of the dienes (vide supra).

The structure of the bicyclic lactones **8a**, **c** deserves comment. Their ^{1}H NMR, COSY, and ^{13}C NMR spectra firmly revealed the existence of a bicyclolactone skeleton. However, if the first cyclization occurs on an oxygen atom of the carboxamide moiety of acetoacetamide, an acyl group should remain at the C-1 position of the bicyclolactones. On the contrary, their IR and ^{13}C NMR spectra did not show the presence of an acyl group, but, rather, an acetoxyl group introduced in the side chain at C-8. Moreover, the configuration of H-1, H-5, and H-8 was all *cis* position according to an NOE difference experiment (Fig. 4).[21)] We cannot explain the deacylation mechanism at this moment; this unexpected reaction was not pursued further in view of the radical cyclization.[22)]

The reaction of 1,1,5,5-tetraaryl-1,4-pentadienes **10a**—**c** with acetoacetamide was more complicated. Only substituted 1,4-pentadienes **11a**—**c** and 4-(2-propenyl)-4,5-dihydrofurans **12a**—**c** were obtained as isolable compounds in yields as shown in Table 3. In the reaction of **10c** a small amount of methylenebisdihydrofuran **13** was also obtained (Entry 21).[1)] When **10b** was allowed to react with acetoacetamide under similar conditions, lactam **14** was formed in addition to **11b** and **12b** (Entry 20). A characteristic feature of **14** was

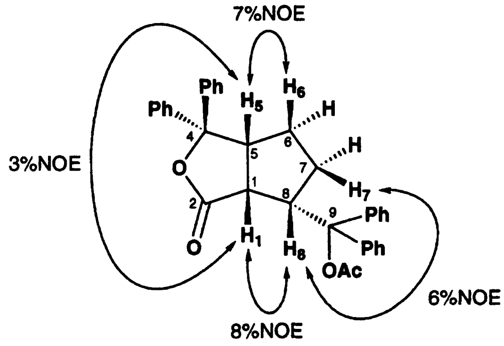


Fig. 4. NOE difference experiment of **8a**.

Table 3. Reaction of 1,4-Pentadienes **10a**—**c** with Acetoacetamide in the Presence of Manganese(III) Acetate[a)]

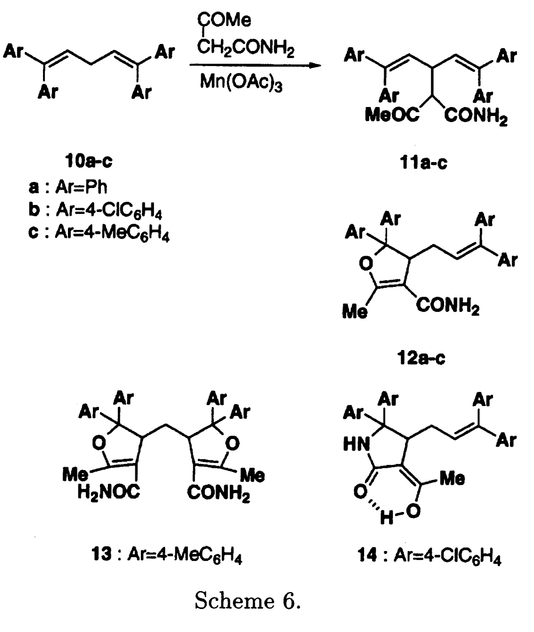
Entry	1,4-Pentadiene	Molar ratio[b)]	Conversion of 1,4-pentadiene/%	Product(yield/%)[c)]		
18	**10a**	3 : 1 : 3	52[d)]	**11a** (23)[e)]	**12a** (26)[e,f)]	
19	**10a**	1 : 4 : 4	91	**11a** (25)	**12a** (18)[f)]	
20	**10b**	1 : 6 : 5	95	**11b** (18)	**12b** (22)	**14** (12)
21	**10c**	1 : 6 : 5	77	**11c** (26)	**12c** (20)	**13** (3)

a) The reaction was carried out in boiling acetic acid (30 mL) for 1 min. b) 1,4-Pentadiene (0.5 mmol) : acetoacetamide : manganese(III) acetate. c) Isolated yield based on the pentadiene added. d) The conversion based on the acetoacetamide added. e) Isolated yield based on the acetoacetamide added. f) A trace amount of 2-acetoxy-1,1,5,5-tetraphenyl-1,4-pentadiene was also isolated.

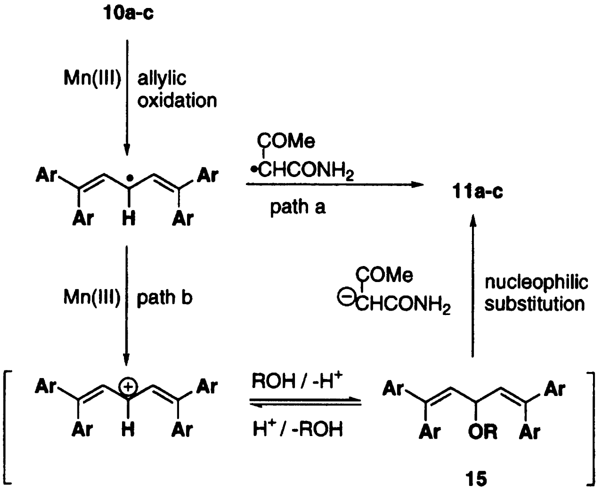
that the compound existed as an enolate form based on the IR and NMR spectra (Scheme 6). The complexity of the reaction seems to depend on the length of the carbon chain. If subsequent intramolecular cyclization of monocyclic compounds, such as **12a**—**c** and **14**, occurred, thermodynamically unstable bicyclic or tricyclic compounds would be formed. Furthermore, a ready allylic oxidation of **10a**—**c** also complicated the reaction because the substituted compounds **11a**—**c** were subject to further oxidation.

It is noteworthy that the allylic oxidative substitution occurred and gave **11a**—**c** (Entries 18—21). We recently reported that oxidation of xanthenes with manganese(III) acetate in the presence of 1,3-dicarbonyl compounds gave 2-(9-xanthenyl)-1,3-dicarbonyl compounds, and proposed both a radical pathway involving 1-carbamoyl-2-oxopropyl radicals and a nucleophilic substitution pathway involving 1-carbamoyl-2-oxopropanide ions complexed to Mn(II) or Mn(III) acetate.[13f] In order to elucidate the allylic oxidation mechanism, 3-alkoxy-1,4-pentadiene (**15**, R=Et) was synthesized[23] and allowed to react in the presence of acetoacetamide and manganese(II) acetate. The result was very clear, and we obtained **11a** quantitatively (see Experimental). This fact supports the supposition that the substituted 1,4-pentadienes **11a**—**c** were formed via nucleophilic substitution with acetoacetamide anions (path b in Scheme 7).

In summary, we have demonstrated a manganese(III)-mediated radical cyclization of 1,ω-alkadienes with malonamide that promises to have applications to the synthesis of azabicyclic and polyquinane skeletons.[24,25] We have also showed that 1,1,6,6-tetrasubstituted 1,5-hexadienes, having electron-donating aryl groups, were inclined to produce azabicyclic compounds preferentially. We will discuss a range of substituent effects, especially on radical sources such as *N*-substituted malonamide derivatives, and potential applications to synthetic targets in a following paper.



Scheme 6.



Scheme 7.

Experimental

General. All melting points were determined using a Yanaco micromelting point apparatus and are uncorrected. NMR spectra were recorded at 60, 90, or 400 MHz for ^{1}H and at 22.4 or 100 MHz for ^{13}C in $CDCl_3$, except where otherwise indicated. The chemical shifts are reported in δ (ppm) and the coupling constants in J (hertz). IR spectra were recorded in $CHCl_3$, except where otherwise stated, and are expressed in ν (cm^{-1}). Mass spectra were obtained at an ionization energy of 70 eV. Compounds for which an exact mass is reported exhibited no significant peaks at m/z greater than that of the parent. Combustion analyses were performed by Elemental Analysis Center, Faculty of Pharmacy, Kumamoto University, Japan.

Materials. Manganese(III) acetate, [$Mn(OAc)_3$], was prepared according to a previously discribed method.[26] 1,1,6,6-Tetrasubstituted 1,5-hexadienes (**1a**—**e**), 1,1,5,5-tetrasubstituted 1,4-pentadienes (**10a**—**c**), and 1,1,7,7-tetrasubstituted 1,6-heptadienes were prepared by dehydration of the corresponding diols, which were synthesized from diethyl adipate (Nacalai Tesque), diethyl glutarate (Tokyo Kasei), and diethyl pimelate (Merck), respectively, and the corresponding arylmagnesium bromide.[1] All of the terminal dienes were purified by recrystallization or medium-pressure liquid-chromatography separation (Fuji Davison FL60D silica gel). Malonamide (Wako), acetoacetamide (Aldrich), manganese(II) acetate tetrahydrate (Wako), anhydrous copper(II) acetate (Wako), selenium(IV) oxide (Wako), and glacial acetic acid (Kanto) were used as received.

Manganese(III)-Mediated Reaction of 1,1,6,6-Tetraaryl-1,5-hexadienes (1a—e) with Malonamide. After a mixture of a hexadiene (0.5 mmol) and malonamide (1-3 mmol) was dissolved in boiling glacial acetic acid (30 mL), manganese(III) acetate (1.5 —4 mmol) was added and continually heated under reflux until the brown color of [$Mn(OAc)_3$] turned transparent brown or yellow. The solvent was removed in vacuo, and the residue was triturated with

2 M hydrochloric acid (30 mL, 1 M=1 mol dm^{-3}) and then extracted with chloroform. The extract was washed with a saturated aqueous solution of sodium hydrogencarbonate and concentrated to dryness. The products were separated on silica-gel TLC (Wakogel B-10 or Whatman K6F silica gel 60A) with diethyl ether–chloroform (2 : 8 v/v) as the developing solvent. The molar ratios, reaction times, and product yields are summarized in Table 1. Analytical samples were further purified by recrystallization from an appropriate solvent, except for liquid products.

1-Carbamoyl-8-(diphenylmethylene)-4,4-diphenyl-3-azabicyclo[3.3.0]octan-2-one (2a): R_f=0.59; colorless microcrystals (from $CHCl_3$/EtOH); mp over 300 °C; IR ($CHCl_3$) ν 3500, 3400 (NH_2), 3184 (NH), 1687 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=1.20—2.70 (4H, m, 2×CH_2), 4.40 (1H, t, J=8.0 Hz, $\rangle$CH–), 4.70 (1H, bs, NH_2), 5.60 (1H, bs, NH_2), 6.80—7.60 (20H, m, arom H), 9.10 (1H, bs, NH); ^{13}C NMR ($CDCl_3$) δ=176.0, 172.5 (C=O), 145.1, 144.1, 143.0, 140.9, 140.3, 139.0 (arom C and $\rangle$C=), 130.2, 128.3, 127.7, 127.2, 127.0, 126.5, 126.2, 126.1 (arom CH), 68.5, 66.1 ($\rangle$C$\langle$), 55.7 ($\rangle$CH–), 33.8, 28.9 (CH_2); MS m/z (rel intensity) 484 (M^+; 100), 441 (86), 260 (50), 215 (39), 182 (86), 165 (26), 104 (19), 77 (17). Found: C, 81.76; H, 5.82; N, 5.77%. Calcd for $C_{33}H_{28}N_2O_2$: C, 81.79; H, 5.82; N, 5.78%.

8-[Bis(4-fluorophenyl)methylene]-1-carbamoyl-4,4-bis(4-fluorophenyl)-3-azabicyclo[3.3.0]octan-2-one (2b): R_f = 0.33; colorless microcrystals (from $CHCl_3$/EtOH); mp 180—185 °C; IR ($CHCl_3$) ν 3512, 3404 (NH_2), 3168 (NH), 1690 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=1.00—2.83 (4H, m, 2×CH_2), 4.00—4.40 (1H, m, $\rangle$CH–), 5.00—5.60 (2H, bs, NH_2), 6.57—7.80 (16H, m, arom H), 8.93 (1H, bs, NH); MS m/z (rel intensity) 556 (M^+; 100), 513 (60), 310 (20), 296 (45), 218 (50), 203 (32). HRMS Found: m/z 556.1733. Calcd for $C_{33}H_{24}F_4N_2O_2$: M, 556.1774.

8-[Bis(4-chlorophenyl)methylene]-1-carbamoyl-4,4-bis(4-chlorophenyl)-3-azabicyclo[3.3.0]octan-2-one (2c): R_f = 0.53; colorless microcrystals (from $CHCl_3$/EtOH); mp 190—192 °C; IR ($CHCl_3$) ν 3520, 3430 (NH_2), 1700, 1690 cm^{-1} (C=O); ^{1}H NMR (DMSO-d_6) δ= 0.70—2.10 (4H, m, 2×CH_2), 4.15 (1H, t, J=7.5 Hz, $\rangle$CH–), 6.55 (2H, bs, NH_2), 7.00—7.90 (16H, m, arom H), 9.55 (1H, bs, NH). Found: C, 63.43; H, 3.87; N, 4.42%. Calcd for $C_{33}H_{24}Cl_4N_2O_2$: C, 63.69; H, 3.89; N, 4.50%.

8-[Bis(4-methylphenyl)methylene]-1-carbamoyl-4,4-bis(4-methylphenyl)-3-azabicyclo[3.3.0]octan-2-one (2d): Colorless microcrystals (from $CHCl_3$/EtOH); mp 165—167 °C; IR ($CHCl_3$) ν 3504, 3408 (NH_2), 3180 (NH), 1715, 1685 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=1.00—2.50 (4H, m, 2×CH_2), 2.13 (3H, s, Me), 2.20 (3H, s, Me), 2.23 (3H, s, Me), 2.30 (3H, s, Me), 4.30 (1H, t, J=8.0 Hz, $\rangle$CH–), 4.50—5.10 (1H, bs, NH_2), 5.20—6.10 (1H, bs, NH_2), 6.80—7.50 (16H, m, arom H), 9.00 (1H, bs, NH). Found: C, 82.12; H, 6.55; N, 5.00%. Calcd for $C_{37}H_{36}N_2O_2$: C, 82.19; H, 6.71; N, 5.18%.

8-[Bis(4-methoxyphenyl)methylene]-1-carbamoyl-4,4-bis(4-methoxyphenyl)-3-azabicyclo[3.3.0]octan-2-one (2e): R_f = 0.19; colorless microcrystals (from $CHCl_3$/hexane); mp 158—159 °C; IR ($CHCl_3$) ν 3500, 3400 (NH_2), 3180 (NH), 1687 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=1.10—2.80 (4H, m, 2×CH_2), 3.53 (3H, s, MeO), 3.65 (3H, s, MeO), 3.73 (3H, s, MeO), 3.78 (3H, s, MeO), 4.30 (1H, t, J=7.0 Hz, $\rangle$CH–), 5.20 (1H, bs, NH_2), 5.80 (1H, bs, NH_2), 6.43—7.56 (16H, m, arom H), 9.53 (1H, bs, NH). Found: C, 73.49; H, 6.19; N, 4.68%. Calcd for $C_{37}H_{36}N_2O_6$: C, 73.49; H, 6.00; N, 4.63%.

7-Acetoxy-1-carbamoyl-8-(diphenylmethylene)-4,4-diphenyl-3-azabicyclo[3.3.0]octan-2-one (3a): R_f=0.23; colorless microcrystals (from $CHCl_3$/EtOH); mp 177—179 °C; IR ($CHCl_3$) ν 3508, 3400 (NH_2), 3184 (NH), 1692 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=1.52 (1.5H, s, OAc), 1.87 (1.5H, s, OAc), 1.20—2.20 (2H, m, CH_2), 4.46, 4.49 (1H, t, J=9.0 Hz, $\rangle$CH–), 5.32 (0.5H, t, J=3.4 Hz, $\rangle$CH–), 4.88, 5.52 (2H, bs, NH_2), 5.85 (0.5H, t, J=7.3 Hz, $\rangle$CH–), 6.80—7.60 (20H, m, arom H), 9.65 (1H, bs, NH); ^{13}C NMR ($CDCl_3$) δ=175.7, 175.5 (C=O), 171.6, 171.1 (C=O), 170.0, 169.6 (C=O), 148.4, 146.4, 144.6, 144.2, 142.6, 142.3, 140.2, 140.1, 137.2, 136.4 (arom C and $\rangle$C=), 129.9, 129.1, 128.6, 128.3, 127.0, 126.1, 125.6 (arom CH), 75.6, 75.1 ($\rangle$CH–O), 68.8, 68.3, 67.2, 66.4 ($\rangle$C$\langle$), 53.4, 51.4 ($\rangle$CH–), 36.3, 35.3 (CH_2), 21.0, 20.3 (Me); MS m/z (rel intensity) 542 (M^+; 39), 499 (21), 483 (25), 439 (84), 274 (100), 257 (80), 229 (70), 215 (24), 182 (99), 167 (29), 104 (20), 77 (15). Found: C, 77.40; H, 5.65; N, 5.27%. Calcd for $C_{35}H_{30}N_2O_4$: C, 77.47; H, 5.57; N, 5.16%.

7-Acetoxy-8-[bis(4-fluorophenyl)methylene)]-1-carbamoyl-4,4-bis(4-fluorophenyl)-3-azabicyclo[3.3.0]octan-2-one (3b): R_f=0.20; colorless microcrystals (from $CHCl_3$/EtOH); mp 250—253 °C; IR ($CHCl_3$) ν 3504, 3396 (NH_2), 3160 (NH), 1730 (OAc), 1691 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=1.00—2.50 (2H, m, CH_2), 1.60 (1.4H, s, OAc), 1.93 (1.6H, s, OAc), 4.10—4.70 (1H, m, $\rangle$CH–), 5.17—5.67 (2H, bs, NH_2), 5.37 (0.53H, t, J=3.0 Hz, $\rangle$CH–), 5.87 (0.47H, t, J=7.0 Hz, $\rangle$CH–), 6.47—7.38 (16H, m, arom H), 9.40 (1H, bs, NH); MS m/z (rel intensity) 614 (M^+; 100), 571 (45), 555 (12), 529 (27), 511 (23), 467 (10), 310 (26), 294 (75), 265 (17), 218 (68), 203 (24). HRMS Found: m/z 614.1835. Calcd for $C_{35}H_{26}F_4N_2O_4$: M, 614.1829.

7-Acetoxy-8-[bis(4-chlorophenyl)methylene)]-1-carbamoyl-4,4-bis(4-chlorophenyl)-3-azabicyclo[3.3.0]octan-2-one (3c): R_f=0.36; colorless microcrystals (from $CHCl_3$/EtOH); mp 219—221 °C; IR (KBr) ν 3470, 3400 (NH_2), 3200 (NH), 1740 (OAc), 1689 cm^{-1} (C=O); ^{1}H NMR (DMSO-d_6) δ=1.10—1.70 (2H, m, CH_2), 2.00 (3H, s, OAs), 4.35 (1H, m, $\rangle$CH–), 5.00 (1H, m, $\rangle$CH–), 5.80 (1H, bs, NH_2), 6.80 (1H, bs, NH_2), 7.10—7.90 (16H, m, arom H), 9.65 (1H, bs, NH). Found: C, 61.52; H, 3.90; N, 4.11%. Calcd for $C_{35}H_{26}Cl_4N_2O_4$: C, 61.78; H, 3.85; N, 4.12%.

8-[Bis(4-methylphenyl)methylene]-1-carbamoyl-4,4-bis(4-methylphenyl)-3-oxabicyclo[3.3.0]octan-2-one (4d): Colorless microcrystals (from $CHCl_3$/EtOH); mp 257—258 °C; IR ($CHCl_3$) ν 3516, 3464 (NH_2), 1762, 1687 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=1.20—2.70 (4H, m, 2×CH_2), 2.20 (3H, s, Me), 2.23 (3H, s, Me), 2.25 (3H, s, Me), 2.30 (3H, s, Me), 4.38 (1H, dd, J=8.0, 9.0 Hz, $\rangle$CH–), 4.50—5.30 (2H, bs, NH_2), 6.80—7.70 (16H, m, arom H). Found: C, 81.75; H, 6.43; N, 2.58%. Calcd for $C_{37}H_{35}NO_3$: C, 82.04; H, 6.51; N, 2.59%.

4,4,9,9-Tetraphenyl-3,10-dioxatricyclo[6.3.0.0^{1,5}]undecane-2,11-dione (5a): R_f=0.62 ($CHCl_3$); colorless microcrystals (from $CHCl_3$/hexane); mp 255—256 °C, (lit,[11c] mp 248—249 °C); IR ($CHCl_3$) ν 1790, 1766 cm^{-1}

(C=O); ^{1}H NMR ($CDCl_3$) δ=1.10—1.90 (4H, m, 2×CH_2), 4.10 (2H, m, 2×$\rangle$CH–), 7.10—7.73 (20H, m, arom H).

4,4,9,9-Tetrakis(4-fluorophenyl)-3,10-dioxatricyclo[6.3.0.0^{1,5}]undecane-2,11-dione (5b): R_f=0.68 ($CHCl_3$); colorless microcrystals (from $CHCl_3$/EtOH); mp 133—135 °C; IR ($CHCl_3$) ν 1790, 1771 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=1.10—2.00 (4H, m, 2×CH_2), 3.83—4.33 (2H, m, 2×$\rangle$CH–), 6.80—7.77 (16H, m, arom H). Found: C, 70.99; H, 4.03%. Calcd for $C_{33}H_{22}F_4O_4$: C, 70.96; H, 3.97%.

4,4,9,9-Tetrakis(4-chlorophenyl)-3,10-dioxatricyclo[6.3.0.0^{1,5}]undecane-2,11-dione (5c): Colorless microcrystals (from $CHCl_3$/hexane); mp 255—256 °C; IR ($CHCl_3$) ν 1796, 1775 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ= 1.10—1.45 (2H, m, CH_2), 1.55—1.90 (2H, m, CH_2), 4.00 (2H, t, J=7.5 Hz, 2×$\rangle$CH–), 7.10—7.67 (16H, m, arom H); ^{13}C NMR ($CDCl_3$) δ=170.6 (C=O); 141.5, 139.6, 134.5, 134.0 (arom C), 128.9, 128.8, 127.3, 126.3 (arom CH), 89.6 ($\rangle$C–O), 65.6 ($\rangle$C$\langle$), 56.2 ($\rangle$CH–), 32.6 (CH_2); MS m/z (rel intensity) 624 (M$^+$; 20), 622 (M$^+$; 15), 328 (12), 293 (16), 139 (17), 94 (100). Found: C, 63.12; H, 3.62%. Calcd for $C_{33}H_{22}Cl_4O_4$: C, 63.48; H, 3.55%.

4,4,9,9-Tetrakis(4-methylphenyl)-3,10-dioxatricyclo[6.3.0.0^{1,5}]undecane-2,11-dione (5d): R_f=0.58 ($CHCl_3$); colorless microcrystals (from $CHCl_3$/EtOH); mp 217—218 °C; IR ($CHCl_3$) ν 1790, 1763 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=1.10—2.00 (4H, m, 2×CH_2), 2.27 (6H, s, 2×Me), 2.30 (6H, s, 2×Me), 3.83—4.23 (2H, m, 2×$\rangle$CH–), 6.93—7.60 (16H, m, arom H). Found: C, 81.49; H, 6.24%. Calcd for $C_{37}H_{34}O_4$: C, 81.89; H, 6.32%.

4,4,9,9-Tetrakis(4-methylphenyl)-3-aza-10-oxatricyclo[6.3.0.0^{1,5}]undecane-2,11-dione (6d): Brown microcrystals (from $CHCl_3$/hexane); mp 259—260 °C; IR ($CHCl_3$) ν 3188 (NH), 1769, 1699 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=0.67—1.83 (4H, m, 2×CH_2), 2.17 (3H, s, Me), 2.27 (3H, s, Me), 2.30 (6H, s, 2×Me), 3.77—4.17 (2H, m, 2×$\rangle$CH–), 6.80—7.57 (16H, m, arom H), 8.20 (1H, bs, NH). Found: C, 81.81; H, 6.44; N, 2.52%. Calcd for $C_{37}H_{35}NO_3$: C, 82.04; H, 6.51; N, 2.59%.

Oxidation of 2a with Manganese(III) Acetate. In order to elucidate the formation of **3a**, a mixture of **2a** (0.5 mmol) and [Mn(OAc)$_3$] (1.0 mmol) was heated under reflux in glacial acetic acid (30 mL) until the brown color of [Mn(OAc)$_3$] turned transparent (for 8 h). The reaction mixture was worked-up by the procedure previously described to give **2a** (67% recovered) and a complex mixture which did not show the existence of any acetoxyl groups in the ^{1}H NMR spectrum.

Manganese(III)-Mediated Reactions of 1,1,5,5-Tetraaryl-1,4-pentadienes (10a—c) and 1,1,7,7-Tetraaryl-1,6-heptadienes with Malonamide. A mixture of **10a**—**c** (0.5 mmol), malonamide (2—5 mmol), and [Mn(OAc)$_3$] (2—6 mmol) was heated at various temperatures (50—140 °C) in glacial acetic acid (30 mL). After a work-up, however, intractable mixtures were obtained.

A similar reaction of 1,1,7,7-tetrakis(4-chlorophenyl)-1,6-heptadiene (0.5 mmol) with malonamide (4 mmol) in the presence of [Mn(OAc)$_3$] (5 mmol) was carried out in boiling glacial acetic acid (30 mL) to give 4,4,10,10-tetrakis(4-chlorophenyl)-3,11-dioxatricyclo[7.3.0.0^{1,5}]dodecane-2,12-dione (11%): R_f=0.61 (diethyl ether : hexane=5 : 5 v/v); colorless microcrystals (from $CHCl_3$/CH_3OH), mp 297—299 °C; IR ($CHCl_3$) ν 1789, 1772 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ= 0.19—0.76 (2H, m, CH_2), 0.85—2.00 (4H, m, 2×CH_2), 3.78 (2H, t, J=7.0 Hz, $\rangle$CH–), 6.99—7.75 (16H, m, arom H). Found: C, 63.75; H, 3.77%. Calcd for $C_{34}H_{24}Cl_4O_4$: C, 63.97; H, 3.79%.

Manganese(III)-Mediated Reaction of 1,1,6,6-Tetraaryl-1,5-hexadienes (1a, 1c, 1d) with Acetoacetamide. To a heated solution of a 1,5-hexadiene (0.5 mmol) and acetoacetamide (1-2 mmol) in glacial acetic acid (30 mL), [Mn(OAc)$_3$] (2—3 mmol) was added. The solution was heated under reflux for 1 min; the solvent was then removed under reduced pressure. The resulting residue was worked-up by the mentioned previously procedure. TLC separations were performed using diethyl ether-hexane (7 : 3 v/v) as the developing solvent to give **7a**,**c**,**d**; **8a**,**c**; **9a**,**c**,**d**. The molar ratios and product distributions are summarized in Table 2.

1-Acetyl-8-diphenylmethylene-4,4-diphenyl-3-azabicyclo[3.3.0]octan-2-one (7a): Colorless microcrystals (from $CHCl_3$/hexane); mp over 300 °C; IR ($CHCl_3$) ν 3180 (NH), 1690 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=0.98 (3H, s, Ac), 1.25—1.90 (2H, m, CH_2), 2.23—3.00 (2H, m, CH_2), 4.22 (1H, dd, J=7.5, 10.0 Hz, $\rangle$CH–), 6.86—7.60 (20H, m, arom H), 10.30 (1H, bs, NH); ^{13}C NMR ($CDCl_3$) δ=208.2, 175.7 (C=O), 144.7, 143.7, 143.0, 141.3, 140.9, 140.1 (arom C and $\rangle$C=), 131.1, 128.5, 128.4, 128.3, 128.0, 127.0, 126.6, 126.5, 126.1, 125.3 (arom CH), 73.9, 68.0 ($\rangle$C$\langle$), 57.9 ($\rangle$CH–), 34.2, 29.2 (CH_2), 28.4 (Me). Found: C, 84.24; H, 6.02; N, 3.00%. Calcd for $C_{34}H_{29}NO_2$: C, 84.44; H, 6.04; N, 2.89%.

8-[Acetoxy(diphenyl)methyl]-4,4-diphenyl-3-oxabicyclo[3.3.0]octan-2-one (8a): R_f=0.72; colorless microcrystals (from $CHCl_3$/MeOH); mp 207—208 °C; IR ($CHCl_3$) ν 1767, 1639 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=1.05—1.38 (2H, m, CH_2), 1.74—2.00 (2H, m, CH_2), 2.08 (3H, s, OAc), 2.49 (1H, dt, J=6.6, 11.7 Hz, H-8), 3.15 (1H, dd, J=6.6, 8.1 Hz, H-1), 4.47 (1H, dt, J=8.1, 2.2 Hz, H-5), 7.10—7.70 (20H, m, arom H); ^{13}C NMR ($CDCl_3$) δ=178.2, 168.7 (C=O), 143.2, 142.8, 142.0 (arom C), 128.5, 128.4, 128.2, 128.0, 127.9, 127.7, 127.6, 127.2, 125.8, 124.8 (arom CH), 88.7, 88.3 ($\rangle$C$\langle$), 50.7, 49.2, 46.1 ($\rangle$CH–), 28.1, 27.0 (CH_2), 22.2 (Me). Found: C, 81.25; H, 6.02%. Calcd for $C_{34}H_{30}O_4$: C, 80.97; H, 5.87%.

Manganese(III)-Mediated Reaction of 1,1,5,5-Tetraaryl-1,4-pentadienes (10a—c) with Acetoacetamide. A mixture of a pentadiene (0.5 mmol), acetoacetamide (2—3 mmol), and glacial acetic acid (30 mL) was heated in a 100-mL round-bottomed flask. Just before refluxing, [Mn(OAc)$_3$] (2—2.5 mmol) was added to the mixture. The mixture was heated under reflux for 1 min. The solvent was removed in vacuo, and the resulting residue was treated by the previously described procedure. TLC separations were carried out using diethyl ether–hexane (8 : 2 v/v) as the developing solvent to yield **11a**—**c**, **12a**—**c**, **13**, and **14**. Product **13** was further purified by TLC with acetone–benzene (6 : 4 v/v) as the developing solvent. The molar ratios and product yields are summarized in Table 3.

2-Acetyl-3-(2,2-diphenylethenyl)-5,5-diphenyl-4-pentenamide (11a): R_f=0.60; yellow liquid; IR ($CHCl_3$) ν 3500, 3356 (NH_2), 1678 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=1.80 (3H, s, Ac), 3.60 (1H, d, J=6.0 Hz, $\rangle$CH–), 3.93 (1H, dt, J=6.0, 10.0 Hz, $\rangle$CH–), 5.68 (1H, bs, NH_2), 6.10

(1H, d, J=10.0 Hz, =CH–), 6.17 (1H, d, J=10.0 Hz, =CH–), 6.75 (1H, bs, NH_2), 6.83—7.53 (20H, m, arom H); ^{13}C NMR ($CDCl_3$) δ=206.5, 169.1 (C=O), 143.6, 142.5, 142.3, 142.2, 139.1, 138.8 (arom C and >C=), 129.7, 129.5, 128.4, 128.1, 127.5, 127.3, 127.1, 125.9 (arom CH and =CH–), 64.8, 40.9 (>CH–), 30.6 (Me); MS m/z (rel intensity) 471 (M^+; 15), 428 (100), 371 (54), 293 (33), 191 (34), 167 (96), 115 (15), 91 (40). HRMS Found: m/z 471.2205. Calcd for $C_{33}H_{29}NO_2$: M, 471.2198.

2-Acetyl-3-[2,2-bis(4-chlorophenyl)ethenyl]-5,5-bis(4-chlorophenyl)-4-pentenamide (11b): R_f=0.37; yellow liquid; IR ($CHCl_3$) ν 3504, 3420 (NH_2), 1679 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=2.02 (3H, s, Ac), 3.56 (1H, d, J=8.0 Hz, >CH–), 3.83 (1H, dt, J=8.0, 9.0 Hz, >CH–), 5.62 (1H, bs, NH_2), 5.96 (1H, d, J=9.0 Hz, =CH–), 6.00 (1H, d, J=9.0 Hz, =CH–), 6.55 (1H, bs, NH_2), 6.70—7.60 (16H, m, arom H); MS m/z (rel intensity) 609 (M^+; 23), 566 (100), 509 (55), 363 (30), 235 (56), 165 (20), 139 (29). HRMS Found: m/z 609.0610. Calcd for $C_{33}H_{25}{}^{35}Cl_3{}^{37}ClNO_2$: M, 609.0618.

2-Acetyl-3-[2,2-bis(4-methylphenyl)ethenyl]-5,5-bis(4-methylphenyl)-4-pentenamide (11c): R_f=0.45; yellow liquid; IR ($CHCl_3$) ν 3504, 3412 (NH_2), 1677 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=1.97 (3H, s, Ac), 2.40 (6H, s, 2×Me), 2.47 (3H, s, Me), 2.50 (3H, s, Me), 3.73 (1H, d, J=7.0 Hz, >CH–), 4.13 (1H, dt, J=7.0, 10.0 Hz, >CH–), 6.00 (1H, bs, NH_2), 6.27 (1H, d, J=10.0 Hz, =CH–), 6.33 (1H, d, J=10.0 Hz, =CH–), 6.95 (1H, bs, NH_2), 7.10—7.73 (16H, m, arom H); MS m/z (rel intensity) 527 (M^+; 26), 484 (74), 427 (100), 335 (23), 285 (10), 243 (15), 219 (24), 195 (50), 165 (9), 105 (14). HRMS Found: m/z 527.2767. Calcd for $C_{37}H_{37}NO_2$: M, 527.2824.

3-Carbamoyl-4-(3,3-diphenyl-2-propenyl)-2-methyl-5,5-diphenyl-4,5-dihydrofuran (12a):[1)] R_f=0.23; yellow liquid; IR ($CHCl_3$) ν 3538, 3420 (NH_2), 1669 (C=O), 1627 cm^{-1} (C=C); ^{1}H NMR ($CDCl_3$) δ=2.20—2.47 (2H, m, CH_2), 2.30 (3H, s, Me), 3.60 (1H, t, J=6.0 Hz, >CH–), 4.86 (2H, bs, NH_2), 5.53 (1H, t, J=8.0 Hz, =CH–), 6.97—7.80 (20H, m, arom H); ^{13}C NMR ($CDCl_3$) δ=166.9 (C=O), 164.5 (=C–O), 144.7, 142.8, 142.6, 140.9, 140.0 (arom C and >C=), 129.9, 128.6, 128.1, 128.0, 127.9, 127.8, 127.4, 127.1, 127.0, 126.6, 126.0 (arom CH and =CH–), 109.1 (>C=), 94.0 (>C–O), 51.7 (>CH–), 31.3 (CH_2), 14.5 (Me); MS m/z (rel intensity) 471 (M^+; 3), 277 (100), 232 (19), 193 (18), 165 (13), 115 (22), 91 (10). HRMS Found: m/z 471.2202. Calcd for $C_{33}H_{29}NO_2$: M, 471.2198.

4-[3,3-Bis(4-methylphenyl)-2-propenyl]-3-carbamoyl-2-methyl-5,5-bis(4-methylphenyl)-4,5-dihydrofuran (12c):[1)] R_f=0.30; yellow liquid; IR ($CHCl_3$) ν 3532, 3420 (NH_2), 1666 (C=O), 1626 cm^{-1} (C=C); ^{1}H NMR ($CDCl_3$) δ=2.00—2.55 (2H, m, CH_2), 2.25 (3H, s, Me), 2.30 (3H, s, Me), 2.31 (3H, s, Me), 2.32 (3H, s, Me), 2.40 (3H, s, Me), 3.47 (1H, dd, J=5.0, 7.0 Hz, >CH–), 4.70 (2H, bs, NH_2), 5.22 (1H, t, J=7.0 Hz, =CH–), 6.90—7.40 (16H, m, arom H); MS m/z (rel intensity) 527 (M^+; 15), 305 (71), 260 (34), 221 (100), 195 (26), 105 (18). HRMS Found: m/z 527.2801. Calcd for $C_{37}H_{37}NO_2$: M, 527.2824.

Bis[4-carbamoyl-5-methyl-2,2-bis(4-methylphenyl)-2,3-dihydro-3-furyl]methane (13):[1)] R_f=0.28 (diethyl ether); colorless microcrystals (from $CHCl_3$/hexane); mp 255—258 °C; IR ($CHCl_3$) ν 3480, 3408 (NH_2), 1660 (C=O), 1632 cm^{-1} (C=C); ^{1}H NMR ($CDCl_3$) δ=0.82 (2H, t, J=6.3 Hz, CH_2), 2.20 (6H, s, 2×Me), 2.28 (6H, s, 2×Me), 2.30 (6H, s, 2×Me), 4.15 (2H, t, J=6.3 Hz, 2×>CH–), 6.20 (4H, bs, 2×NH_2), 6.68—7.45 (16H, m, arom H); ^{13}C NMR ($CDCl_3$) δ=169.0 (C=O), 163.1 (=C–O), 142.0, 138.3, 137.3, 136.3 (arom C), 128.8, 128.3, 126.4, 126.1 (arom CH), 112.0 (>C=), 95.5 (>C–O), 46.4 (>CH–), 39.1 (CH_2), 21.0, 20.9 (Me), 14.9 (Me). Found: C, 78.43; H, 6.47; N, 4.55%. Calcd for $C_{41}H_{42}N_2O_4$: C, 78.56; H, 6.57; N, 4.47%.

4-[3,3-Bis(4-chlorophenyl)-2-propenyl]-5,5-bis(4-chlorophenyl)-3-(1-hydroxyethylidene)pyrrolidin-2-one (14): R_f=0.25; colorless microcrystals (from MeOH); mp 120 °C; IR ($CHCl_3$) ν 3600—3100 (NH and OH), 1669 (C=O), 1631 cm^{-1} (C=C); ^{1}H NMR ($CDCl_3$) δ=2.20 (2H, dd, J=6.2, 7.0 Hz, CH_2), 2.25 (3H, s, Me), 3.67 (1H, t, J=6.2 Hz, >CH–), 5.29 (1H, bs, NH or OH), 5.64 (1H, t, J=7.0 Hz, =CH–), 6.77—7.34 (17H, m, arom H and NH or OH); ^{13}C NMR ($CDCl_3$) δ=166.7, 162.6 (C=O and =COH–), 142.9 (>C=), 140.7, 140.2, 138.7, 137.4, 134.1, 133.5, 133.3, 133.2 (arom C), 131.2, 128.6, 128.5, 128.4, 128.3, 128.2, 127.8, 127.3 (arom CH), 126.6 (–CH=), 109.7 (>C=), 93.2 (>C–N), 50.4 (>CH–), 31.5 (CH_2), 14.6 (Me). Found: C, 64.92; H, 4.17; N, 2.38%. Calcd for $C_{33}H_{25}Cl_4NO_2$: C, 65.04; H, 4.13; N, 2.30%.

Synthesis and Reaction of 15 (R=Et) with Acetoacetamide Anion (1-Carbamoyl-2-oxopropanide Ion). A mixture of **10a** (289.4 mg) and selenium dioxide (1.74 g) was refluxed in 95% ethanol (15 mL) for 24 h.[23)] The solvent was removed and the residue was extracted with chloroform. The extract was washed with a saturated aqueous solution of sodium hydrogencarbonate and separated on silica gel TLC (Wakogel B-10) with chloroform as the developing solvent to give 3-ethoxy-1,1,5,5-tetraphenyl-1,4-pentadiene (**15**: R=Et) (40.6 mg, 13%) and **10a** (212.3 mg, 73% recovered).

Compound **15** (R=Et) (40.6 mg) was allowed to react with acetoacetamide (29.2 mg) in the presence of manganese(II) acetate tetrahydrate (54.2 mg) in boiling glacial acetic acid (5 mL) for 3 min.[13f)] The solvent was removed in vacuo, and the obtained residue was triturated with 2 M hydrochloric acid (5 mL). After the aqueous mixture was extracted with chloroform, the extract was concentrated to yield **11a** (42.8 mg, 100%).

X-Ray Crystallography of 2a. A clear, colorless plate having approximate dimensions of 0.40×0.25×0.15 mm was mounted in a random orientation on a Nicolet R3m/V automatic diffractometer. The radiation used was Mo $K\alpha$ monochromatized by a highly ordered graphite crystal. The final cell constants, as well as other information pertinent to data collection and refinement, are listed in Table 4. The Laue symmetry was determined to be $\bar{1}$, and the space group was shown to be either $P1$ or $P\bar{1}$. The intensities were measured using the omega scan technique, with the scan rate depending on the count obtained in rapid pre-scans of each reflection. Two standard reflections were monitored after every two hours or every 100 data points collected; these showed no significant change. During data reduction Lorentz and polarization corrections were applied; however no absorption correction was made due to the very small absorption coefficient.

Because the unitary structure factors showed centric statistics, space group $P\bar{1}$ was assumed from the outset. The

Table 4. Data Collection and Processing Parameters of **2a**

Space group	$P\bar{1}$ (triclinic)
Cell constants	a=9.205(3) Å
	b=12.481(3) Å
	c=12.811(4) Å
	α=72.48(2)°
	β=88.91(2)°
	γ=69.02(2)°
	V=1304 Å^3
Molecular formula	$C_{33}H_{28}N_2O_2$
Formula weight	484.63
Formula units per cell	Z=2
Density	ρ=1.23 g cm^{-3}
Absorption coefficient	μ=0.72 cm^{-1}
Radiation (Mo $K\alpha$)	λ=0.71073 Å
Collection range	$4° \leq 2\theta \leq 50°$
Scan width	$\Delta\theta = 1.20 + (K_{\alpha 2} - K_{\alpha 1})°$
Scan speed range	1.5 to 15.0° min^{-1}
Total data collected	4525
Independent data, $I > 3\sigma(I)$	2243
Total variables	344
$R = \Sigma \lVert F_o \rvert - \lvert F_c \rVert / \Sigma \lvert F_o \rvert$	0.045
$R_w = [\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2 / \Sigma w \lvert F_o \rvert^2]^{1/2}$	0.033
Weights	$w = \sigma(F)^{-2}$

structure was solved by the SHELXTL direct methods program, which revealed the positions of all of the non-hydrogen atoms. The usual sequence of isotropic and anisotropic refinement was followed, after which all hydrogens attached to carbon were entered in ideal calculated positions and constrained to a riding motion. A single isotropic temperature factor was varied for all of them. Hydrogens attached to nitrogen were located in difference Fourier syntheses and allowed to refine independently. After all shift/esd ratios were less than 0.1, convergence was reached at the agreement factors listed in Table 4. No unusually high correlations were noted between any of the variables in the last cycle of full-matrix least-squares refinement, and the final difference density map showed a maximum peak of about 0.2 eÅ^{-3}. All calculations were made using Nicolet's SHELXTL PLUS (1987) series of crystallographic programs. The atomic coordinates of **2a** as well as other pertinent data have been deposited at the Cambridge Crystallographic Data Centre (CCDC) as well as Document No. 68030 at the Office of the Editor of Bull. Chem. Soc. Jpn. They can be obtained upon request to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

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Supplementary Material Available: Spectral data and the melting points for all compounds not described in the experimental section (2 pages); X-ray crystallographic data consisting of atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, H-atom coordinates and isotropic displacement parameters, hydrogen bonding parameters, and torsion angles for **2a** (7 pages) including least-squares plane numbers (7 pages), and observed and calculated structure factors for **2a** (17 pages); and ^{1}H, ^{13}C NMR, COSY, and NOE difference spectra of **8a** (13 pages) are kept on deposit as Document No. 68030 at the Office of the Editor of Bull. Chem. Soc. Jpn.

References

1) Preceding paper by H. Nishino, T. Yoshida, and K. Kurosawa, *Bull. Chem. Soc. Jpn.*, **64**, 1097 (1991).

2) a) E. J. Enholm, J. A. Burroff, and L. M. Jaramillo, *Tetrahedron Lett.*, **31**, 3727 (1990); b) C. -K. Sha, T. -S. Jean, and D. -C. Wang, *Tetrahedron Lett.*, **31**, 3745 (1990); c) S. Iwasa, M. Yamamoto, S. Kohmoto, and K. Yamada, *J. Org. Chem.*, **56**, 2849 (1991); d) J. Lee, K. Teng, and V. E. Marquez, *Tetrahedron Lett.*, **33**, 1539 (1992); e) A. Ail, D. C. Harrowven, and G. Pattenden, *Tetrahedron Lett.*, **33**, 2851 (1992); f) A. Llebaria, F. Camps, and J. M. Moretó, *Tetrahedron Lett.*, **33**, 3683 (1992); g) J. S. Yadav, T. K. Praveen Kumar, and V. R. Gadgil, *Tetrahedron Lett.*, **33**, 3687 (1992); h) G. Pattenden and D. J. Schulz, *Tetrahedron Lett.*, **34**, 6787 (1993).

3) a) E. J. Corey and X. -M. Cheng, "The Logic of Chemical Synthesis," John Wiley & Sons, New York (1989); b) T. Lindberg, "Strategies and Tactics in Organic Synthesis," Vols. 2 and 3, Academic Press, San Diego (1989, 1990).

4) For review: G. G. Melikyan, *Synthesis*, **1993**, 833.

5) a) M. A. Dombroski, S. A. Kates, and B. B. Snider, *J. Am. Chem. Soc.*, **112**, 2759 (1990), and references cited therein; b) S. A. Kates, M. A. Dombroski, and B. B. Snider, *J. Org. Chem.*, **55**, 2427 (1990); c) D. P. Curran, T. M.

Morgan, C. E. Schwartz, B. B. Snider, and M. A. Dombroski, *J. Am. Chem. Soc.*, **113**, 6607 (1991); d) B. B. Snider, B. Y. Wan, B. O. Buckman, and B. M. Foxman, *J. Org. Chem.*, **56**, 328 (1991); e) B. B. Snider, J. E. Merritt, M. A. Dombroski, and B. O. Buckman, *J. Org. Chem.*, **56**, 5544 (1991); f) B. B. Snider and B. O. Buckman, *J. Org. Chem.*, **57**, 322 (1992); g) B. B. Snider and T. Kwon, *J. Org. Chem.*, **57**, 2399 (1992); h) B. B. Snider, Q. Zhang, and M. A. Dombroski, *J. Org. Chem.*, **57**, 4196 (1992); i) B. B. Snider, N. H. Vo, and B. M. Foxman, *J. Org. Chem.*, **58**, 7228 (1993).

6) M. P. Bertrand, J. -M. Surzur, H. Oumar-Mahamat, and C. Moustrou, *J. Org. Chem.*, **56**, 3089 (1991).

7) P. A. Zoretic, X. Weng, M. L. Caspar, and D. G. Davis, *Tetrahedron Lett.*, **32**, 4819 (1991).

8) J. M. Mellor and S. Mohammed, *Tetrahedron Lett.*, **32**, 7107 (1991); *Tetrahedron Lett.*, **32**, 7111 (1991).

9) C. -P. Chuang and S. -F. Wang, *Tetrahedron Lett.*, **35**, 1283 (1994); *Tetrahedron Lett.*, **35**, 4365 (1994).

10) a) S. Tategami, T. Yamada, H. Nishino, J. D. Korp, and K. Kurosawa, *Tetrahedron Lett.*, **31**, 6371 (1990); b) H. Nishino, S. Tategami, T. Yamada, J. D. Korp, and K. Kurosawa, *Bull. Chem. Soc. Jpn.*, **64**, 1800 (1991); c) C. -Y. Qian, H. Nishino, and K. Kurosawa, *Bull. Chem. Soc. Jpn.*, **64**, 3557 (1991); d) C. -Y. Qian, T. Yamada, H. Nishino, and K. Kurosawa, *Bull. Chem. Soc. Jpn.*, **65**, 1371 (1992); e) T. Yamada, Y. Iwahara, H. Nishino, and K. Kurosawa, *J. Chem. Soc., Perkin Trans. 1*, **1993**, 609; f) C. -Y. Qian, H. Nishino, and K. Kurosawa, *J. Heterocycl. Chem.*, **30**, 209 (1993); g) C. -Y. Qian, H. Nishino, K. Kurosawa, and J. D. Korp, *J. Org. Chem.*, **58**, 4448 (1993).

11) a) N. Ito, H. Nishino, and K. Kurosawa, *Bull. Chem. Soc. Jpn.*, **56**, 3527 (1983); b) N. Fujimoto, H. Nishino, and K. Kurosawa, *Bull. Chem. Soc. Jpn.*, **59**, 3161 (1986); c) W. E. Fristad and S. S. Hershberger, *J. Org. Chem.*, **50**, 1026 (1985); d) W. E. Fristad, J. R. Peterson, and A. B. Ernst, *J. Org. Chem.*, **50**, 3143 (1985).

12) H. Nishino, *Bull. Chem. Soc. Jpn.*, **58**, 217 (1985).

13) For manganese(III) oxidation with alkenes: a) W. E. Fristad and J. R. Peterson, *J. Org. Chem.*, **50**, 10 (1985); b) J. A. Norman, C. B. Thomas, and M. J. Burrow, *J. Chem. Soc., Perkin Trans. 1*, **1985**, 1087; c) W. E. Fristad, J. R. Peterson, A. B. Ernst, and G. B. Urbi, *Tetrahedron*, **42**, 3429 (1986). For manganese(III) oxidation in the presence of active methylene compounds; d) H. Nishino, *Bull. Chem. Soc. Jpn.*, **59**, 1733 (1986); e) H. Nishino, K. Tsunoda, and K. Kurosawa, *Bull. Chem. Soc. Jpn.*, **62**, 545 (1989); f) H. Nishino, H. Kamachi, H. Baba, and K. Kurosawa, *J. Org. Chem.*, **57**, 3551 (1992).

14) a) A. L. J. Beckwith, G. Phillipou, and A. K. Serelis, *Tetrahedron Lett.*, **22**, 2811 (1981); b) A. L. J. Beckwith, D. H. Roberts, C. H. Schiesser, and A. Wallner, *Tetrahedron Lett.*, **26**, 3349 (1985); c) A. L. J. Beckwith and C. H. Schiesser, *Tetrahedron*, **41**, 3925 (1985); d) J. D. Kilburn, *Tetrahedron Lett.*, **31**, 2193 (1990); e) W. B. Motherwell and M. Shioman, *Tetrahedron Lett.*, **32**, 1103 (1991).

15) Fristad and Hershberger also reported similar products obtained from the manganese(III) acetate oxidation of **1a** with malonic acid, but they did not mention their stereochemistry in detail.[11c)]

16) We tried to separate the mixture by TLC (silica gel) and HPLC equipped with an RP-18 ODS column, but we could not isolate the isomers.

17) If the reaction is carried out at 23 °C under current air, 1,2-dioxan-3-ol derivatives will be generally formed and the reaction becomes to be very complicated.

18) a) J. K. Kochi and A. Bemis, *J. Am. Chem. Soc.*, **90**, 4038 (1968); b) J. K. Kochi, A. Bemis, and C. L. Jenkins, *J. Am. Chem. Soc.*, **90**, 4616 (1968); c) J. K. Kochi and J. D. Bacha, *J. Org. Chem.*, **33**, 2746 (1968); d) C. L. Jenkins and J. K. Kochi, *J. Am. Chem. Soc.*, **94**, 843 (1972); e) J. K. Kochi, "Oxidation-Reduction Reactions of Free Radicals and Metal Complexes," in "Free Radicals," ed by J. K. Kochi, John Wiley & Sons, New York (1973), pp. 591—683.

19) H. Sato, H. Nishino, and K. Kurosawa, *Bull. Chem. Soc. Jpn.*, **60**, 1753 (1987).

20) T. -L. Ho, "Hard and Soft Acids and Bases Principle in Organic Chemistry," Academic Press, New York (1977).

21) In order to compare the energy of **8a** with that of the corresponding C-8 anomer, MM2 calculations were conducted. Surprisingly, the conformation of **8a** (33 kcal mol^{-1}) was more stable than that of the C-8 anomer (36 kcal mol^{-1}).

22) The editor suggested one of the possible mechanisms that carboxymethyl radicals, $\cdot CH_2CO_2H$, probably formed by thermolysis of manganese(III) acetate might add one of the double bonds of **1a,c** and mono-γ-lactones might be formed, which subsequently oxidized with manganese(III) acetate to give **8a,c**. However, it is known that 1,3-dicarbonyl radicals preferentially attack double bonds in the manganese(III) acetate-1,3-dicarbonyl compounds system and products derived from carboxymethyl radicals are not detected in the same reaction system.[1,13f)] In fact, oxidation of **1a** with manganese(III) acetate at the molar ratio of 1 : 4 in boiling acetic anhydride–acetic acid for 10 min gave 3-(4,4-diphenyl-3-butenyl)-4,4-diphenylbutanolide (28%) and the corresponding ethylenebis(γ-lactone) (50%) together with **1a** (6%) recovered.[13c)] In addition, 3-(4,4-diphenyl-3-butenyl)-4,4-diphenylbutanolide was oxidized with manganese(III) acetate at the molar ratio of 1 : 2 in boiling acetic acid for 4 h to give the same ethylenebis(γ-lactone) (61%) and the mono γ-lactone unchanged was recovered (35%). Any bicyclic compounds such as **8a,c** were not detected in the both reactions.

23) U. T. Bhalerao and H. Rapoport, *J. Am. Chem. Soc.*, **93**, 4835 (1971).

24) L. A. Paquette and A. M. Doherty, "Polyquinane Chemistry, Syntheses and Reactions," Springer-Verlag, Berlin (1987).

25) E. J. Corey and M. Kang, *J. Am. Chem. Soc.*, **106**, 5384 (1984).

26) E. I. Heiba, R. M. Dessau, and W. J. Koehl, Jr., *J. Am. Chem. Soc.*, **91**, 138 (1969).