Mn(III)-BASED REACTION OF ALKENES WITH PYRROLIDINEDIONE DERIVATIVES. FORMATION OF BICYCLIC PEROXIDES AND THE RELATED COMPOUNDS[1]

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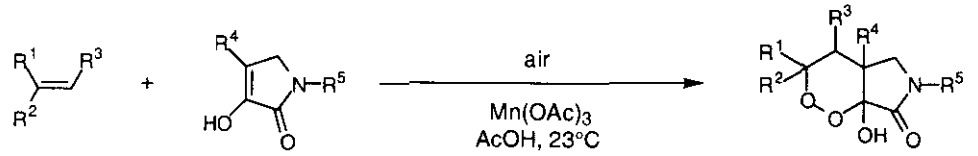
Abstract - Alkenes (**1**) and 2,3-pyrrolidinediones (**2**) were treated with manganese(III) acetate in acetic acid at 23 °C under a stream of dry air giving 1-hydroxy-8-aza-2,3-dioxabicyclo[4.3.0]nonan-9-ones (**3**) in good yields. The reaction at elevated temperature gave 4-ethenyl-2,3-pyrrolidinediones (**6**) and/or 4-alkyl-2,3-pyrrolidinediones (**7**) in good yields. A wide variety of 2,3-pyrrolidinediones having an alkoxycarbonyl, cyano, or acyl group at the 4-position were tested to delineate the scope and limitations of these reactions. The mechanisms for the formation of the products were also discussed.

INTRODUCTION

The Mn(III)-induced oxidative cyclizations have attracted renewed attention in the past decade since they provided a versatile protocol for the formation of highly functionalized products from simple precursors.[2] These cyclizations have been initiated by the reaction of enolizable carbonyl compounds with manganese(III) acetate to form manganese(III) enolates which undergo one-electron transfer to produce carbon radicals and manganese(II). In conjunction with our research program concerning the development of the synthetic methodology for the preparation of cyclic peroxides using manganese complexes,[3] we were intrigued with the possibility of achieving bicyclic peroxides containing both a 1,2-dioxane ring and a lactam ring in a Mn(III)-based formal [2 + 2 + 2] cycloaddition of molecular oxygen, pyrrolidinedione derivatives, and alkenes analogous to that of molecular oxygen, 1,3-diketone, and alkene by electrochemical technique which was first reported by Yoshida et al.[4] A wide variety of biologically active cyclic peroxides were found in marine sponges.[5] Normally, the cyclic peroxides were synthesized according to photooxygenation strategy.[6] For our goal in this paper, 2,3-pyrrolidinediones having an electron-withdrawing substituent at the 4-position appeared to be effective candidates in playing the role of

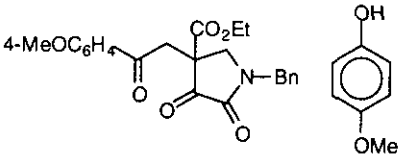
Scheme 1



1a-i **2a-l** **3**

1a: $R^1 = R^2 = Ph$, $R^3 = H$
1b: $R^1 = R^2 = 4\text{-}MeC_6H_4$, $R^3 = H$
1c: $R^1 = R^2 = 4\text{-}MeOC_6H_4$, $R^3 = H$
1d: $R^1 = R^2 = 4\text{-}ClC_6H_4$, $R^3 = H$
1e: $R^1 = R^2 = 4\text{-}FC_6H_4$, $R^3 = H$
1f : $R^1 = Me$, $R^2 = Ph$, $R^3 = H$
1g: $R^1 = R^2 = Me$, $R^3 = H$
1h: $R^1 = R^2 = Et$, $R^3 = H$
1i : R^1, $R^3 = -(CH_2)_6-$, $R^2 = H$

2a: $R^4 = CO_2Et$, $R^5 = Bn$
2b: $R^4 = CO_2Me$, $R^5 = Bn$
2c: $R^4 = CO_2Bu$, $R^5 = Bu$
2d: $R^4 = CO_2Et$, $R^5 = Bu$
2e: $R^4 = CO_2Et$, $R^5 = Et$
2f : $R^4 = CO_2Bu$, $R^5 = Me$
2g: $R^4 = CN$, $R^5 = Et$
2h: $R^4 = CN$, $R^5 = Bu$
2i : $R^4 = CN$, $R^5 = Bn$
2j : $R^4 = COEt$, $R^5 = Bn$
2k: $R^4 = COPr$, $R^5 = Bn$
2l : $R^4 = COPr^i$, $R^5 = Bn$



4 **5**

an enolizable carbonyl compound since they possessed a " free" carbonyl group on the ring, which would allow the formal [2 + 2 + 2] cyclization. We were pleased to find that the reaction of 4-alkoxycarbonyl-, 4-cyano-, or 4-acyl-2,3-pyrrolidinediones, molecular oxygen, and alkenes gave the desired 1-hydroxy-8-aza-2,3-dioxabicyclo[4.3.0]nonan-9-ones in good yields.[1] Recently, it was reported that the pyrrolidinedione derivatives were synthesized as endothelin receptor antagonists.[7] We thus applied the Mn(III)-based reaction to a wide variety of alkenes and 2,3-pyrrolidinediones at both 23 °C and elevated temperature. In this paper, we report the results of our study in detail and discuss the reaction mechanism.

RESULTS AND DISCUSSION

Preparation of Pyrrolidinedione Derivatives. The 2,3-pyrrolidinediones investigated in this study were alkyl 2,3-pyrrolidinedione-4-carboxylates (**2a-f**), 4-cyano-2,3-pyrrolidinediones (**2g-i**), and 4-acyl-2,3-pyrrolidinediones (**2j-l**). The pyrrolidinediones (**2a-f**) were prepared by treatment of alkyl (β-alkylamino)propionates[8] with dialkyl oxalates in the presence of the corresponding sodium alkoxides according to the procedure used for the methyl 1-phenyl-2,3-pyrrolidinedione-4-carboxylate.[9] This procedure was also used to make pyrrolidinediones (**2g-i**) from sodium ethoxide, diethyl oxalate, and β-alkylaminopropionitriles. The latter, in turn, was obtained from amines and acrylonitrile.[10] 4-Acyl-2,3-pyrrolidinediones (**2j-l**) were prepared from methyl acylpyruvates,[11] and methylidenebenzylamine resulted from the normal procedure for the preparation of aldimines.[12] All these pyrrolidinediones exist in the enol form, *i.e.*, as 3-hydroxy-3-pyrroline-2-one derivatives.

Mn(III)-Based Reaction of Alkenes (1a-i) with 2,3-Pyrrolidinediones (2a-l) and Molecular Oxygen at 23 °C. The reaction of alkenes (**1a-i**) with 2,3-pyrrolidinediones (**2a-l**) in the presence of manganese(III) acetate was run under bubbling dry air to produce the expected bicyclic peroxides (**3**) (Scheme 1 and Table 1). 1,1-Disubstituted ethenes gave good results (Entries 1-6, 10-20),

Table 1. Reaction of Alkenes (1a-i) with 2,3-Pyrrolidinediones (2a-l) in the Presence of Manganese(III) Acetate at 23 °C[a]

Entry	Alkene	Pyrrolidinedione	Molar ratio[b]	Time (h)	Product (Yield/%)[c]
1	**1a**	**2a**	1:2:1	12	**3aa** (84)
2	**1b**	**2a**	1:2:1	12	**3ba** (90)
3	**1c**	**2a**	1:2:1	12	**3ca** (61)[d]
4	**1d**	**2a**	1:2:2	16	**3da** (76)
5	**1e**	**2a**	1:2:1	16	**3ea** (61)
6	**1f**	**2a**	1:2:1	12	**3fa** (79)
7	**1g**	**2a**	Excess:1:1[e]	3	**3ga** (73)[f]
8	**1h**	**2a**	3:1:1	12	**3ha** (58)[f]
9	**1i**	**2a**	3:1:1	12	**3ia** (21)[f]
10	**1a**	**2b**	1:2:1	12	**3ab** (82)
11	**1a**	**2c**	1:2:1	12	**3ac** (79)
12	**1a**	**2d**	1:2:1	12	**3ad** (80)
13	**1a**	**2e**	1:2:1	12	**3ae** (80)
14	**1a**	**2f**	1:2:1	12	**3af** (83)
15	**1a**	**2g**	1:2:1	12	**3ag** (70)
16	**1a**	**2h**	1:2:1	12	**3ah** (69)
17	**1a**	**2i**	1:2:1	12	**3ai** (82)
18	**1a**	**2j**	1:2:1	12	**3aj** (74)
19	**1a**	**2k**	1:2:1	12	**3ak**(74)
20	**1a**	**2l**	1:2:1	12	**3al** (75)

[a] The reaction was carried out under bubbling dry air. [b] **1**:**2**:manganese(III) acetate. [c] Isolated yield based on the amount of **1** used. [d] Products (**4**) and (**5**) were also obtained in 18% and 10% yields, respectively. [e] Isobutene (**1g**) was bubbled into the reaction mixture. [f] Yield based on the amount of **2a** used.

especially in the case of **1b** having a methyl group on the aromatic ring (Entry 2). However, the introduction of a methoxy group on the aromatic ring of the ethene promoted the acid-catalyzed decomposition of the peroxide resulting in a decreased yield of **3ca** and the formation of **4** and **5** (Entry 3).[1] Alkyl-substituted ethenes (**1g-i**) were also applicable to this reaction (Entries 7-9). Surprisingly, the gaseous isobutene remarkably shortened the reaction time (Entry 7). The use of cyclooctene led to the formation of tricyclic peroxide in poor yield (Entry 9). In addition, a replacement of the ethoxycarbonyl group in **2a** by a cyano or an acyl group did not cause any dramatic change in the yield of **3** (Entries 15-20).

Mn(III)-Based Reaction of Alkenes (1a-e) with Ethyl 1-Benzyl-2,3-Pyrrolidinedione-4-carboxylate (2a) at Elevated Temperature. In a previous paper,[1] we reported that a similar reaction of **1a** and **2a** at 70 °C under air yielded the two compounds (**6**) and (**7**) in which no molecular oxygen incorporation took place (Table 2, Entry 21). Since the reaction appeared to be a convenient route

Scheme 2

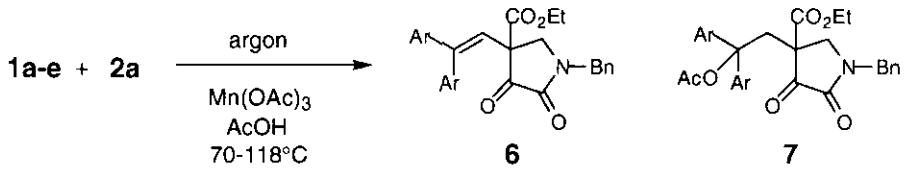


Table 2. Reaction of Alkenes (1a-e) with Ethyl 1-Benzyl-2,3-pyrrolidinedione-4-carboxylate (2a) in the Presence of Manganese(III) Acetate at Elevated Temperature[a]

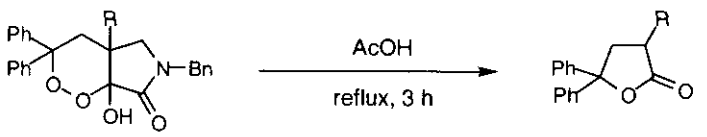
Entry	Alkene	Temperature (°C)	Time (min)	Product (Yield/%)[b]	
21[c]	**1a**	70	10	**6aa** (18)	**7aa** (46)
22	**1a**	70	30	**6aa** (21)	**7aa** (52)
23	**1a**	reflux	2	**6aa** (50)	**7aa** (24)
24	**1b**	70	16	**6ba** (62)	
25	**1b**	reflux	2	**6ba** (79)	
26	**1c**	70	12	**6ca** (87)	
27	**1c**	reflux	1	**6ca** (90)	
28	**1d**	70	40		**7da** (66)
29	**1d**	reflux	2		**7da** (64)
30	**1e**	70	40		**7ea** (45)
31	**1e**	reflux	2	**6ea** (43)	**7ea** (25)

[a] The reaction was carried out in acetic acid at the molar ratio of **1**:**2a**:manganese(III) acetate = 1:3:4 under an argon atmosphere. [b] Isolated yield based on the amount of **1** used. [c] The reaction was conducted under air.

to introduce an alkyl and/or an ethenyl group to the 4-position of 2,3-pyrrolidinediones, we further applied the reaction to other alkenes. Thus, 1,1-diarylethenes (**1a-e**) were allowed to react with **2a** at elevated temperature under an argon atmosphere. In contrast to the reaction at 23 °C in Table 1, the reaction at elevated temperature was remarkably sensitive to the substituent on the aromatic ring (Table 2). While the reaction of **1a** afforded both **6** and **7** in moderate yields, only **6** was obtained in good yield in a similar reaction of **1b, c** (Entries 22-27). On the other hand, the presence of a chlorine atom on the aromatic ring resulted in the formation of **7** (Entries 28, 29). Finally, the reaction of **1e** apparently depended on the reaction temperature (Entries 30, 31).

Acid-Catalyzed Decomposition of Bicyclic Peroxides (3aa, 3ai, and 3ca). Although it was reported that 1,2-dioxan-3-ols were easily decomposed by acid to give furans,[13] stirring **3ca** in acetic acid at 23 °C for 16 h afforded ketone (**4**) (16 %) and phenol (**5**) (15%) along with recovered **3ca** (83%).[1] Surprisingly, refluxing **3aa** in acetic acid for 3 h gave neither the corresponding **4** or **5** but butanolide (**8a**) in 71% yield. A similar decomposition of **3ai** led to the formation of **8i** in 40% yield (Scheme 3).

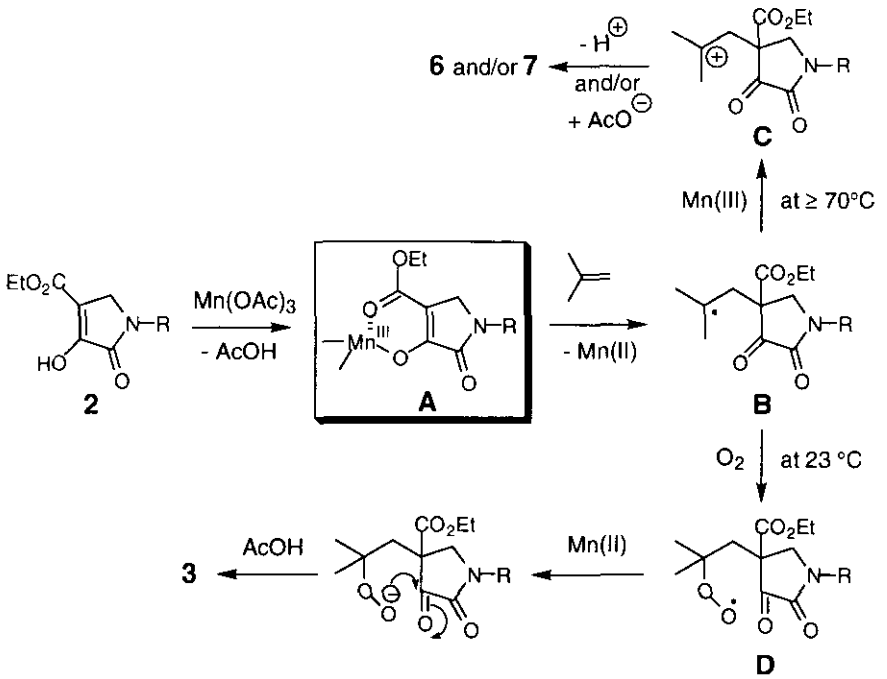
Scheme 3



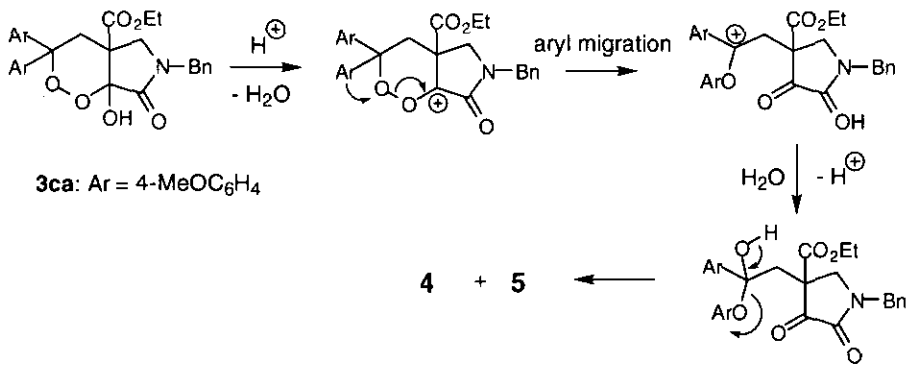
3aa (R = CO_2Et) **8a** (71%)
3ai (R = CN) **8i** (40%)

Mechanisms. When a catalytic amount of manganese(III) acetate was used in the reaction of **1a** with **2a** at 23 °C under air, **3aa** was actually produced in moderate yield.[3d] However, the reaction time was required more than 24 h. Therefore, a stoichiometric amount of manganese(III) acetate was employed in the formal [2 + 2 +2] cycloaddition. The formation of **3**, **6**, and **7** could be explained according to the mechanism outlined in Scheme 4. Complexes similar to **A** have been reported in the literature.[3b,3d,14,15] After the one-electron transfer oxidation step to form radical **B**,[16] the reaction pathway could depend on the ambient temperature. At 23 °C, radical **B** could trap molecular oxyen to produce peroxyl radical **D**,[4] which would be easily reduced with manganese(II) and cyclized to give 1,2-dioxan-3-ol **3**.[3d] At 70 °C or higher, the Mn(III)-based oxidation of **B** to form carbocation **C** could be predominant since molecular oxygen dissolved in the reaction mixture was neglected.[17] From **C**, a β-proton elimination[17f,18] and an attack of an acetate ion[17c,17e,19] would yield **6** and **7**, respectively.

Scheme 4



Scheme 5



The acid-catalyzed decomposition of **3ca**[1] to give ketone (**4**) and phenol (**5**) (Entry 3) could be responsible for the aryl migration as shown in Scheme 5.[13] However, the mechanism for the formation of γ-lactones (**8**) is not clear at present.

CONCLUSION

It was found that the Mn(III)-based formal [2 + 2 + 2] cycloaddition of molecular oxygen, 2,3-pyrrolidinedione derivatives, and alkenes was a versatile synthetic procedure for bicyclic peroxides containing both a 1,2-dioxane ring and a lactam ring. The one-pot reaction of alkenes with the pyrrolidinedione derivatives in the presence of manganese(III) acetate at 23 °C gave 1-hydroxy-8-aza-2,3-dioxabicyclo[4.3.0]nonan-9-ones which have a pyrrolidinone ring bearing an ester, cyano or acyl group at the 4-position. It is noteworthy that analogs of these compounds were designed to be endothelin receptor antagonists.[7] The reaction was applicable for a wide variety of both alkenes and 2,3-pyrrolidinedione derivatives. The results of similar reactions at elevated temperature provided a simple route to introduce an alkyl group or an ethenyl group to the 4-position of 2,3-pyrrolidinediones.

EXPERIMENTAL SECTION

Measurements. NMR spectra were recorded on a JNM EX400 FT NMR spectrometer at 400 MHz for ^1H and at 100 MHz for ^{13}C with tetramethylsilane being used as the internal standard. Chemical shifts are reported in δ and coupling constants in Hz. The IR spectra were measured on a JASCO A-102 IR spectrophotometer. The IR spectral data are expressed in cm^{-1}. MS spectra were measured on either a Shimadzu GCMS QP2000GF or a JMS-LX1000 mass spectrometer. All of the melting points were determined with a Yanaco micromelting-point apparatus MP-J3 and were uncorrected. Elemental analyses were performed at the Center of Instrumental Analysis, Kumamoto University, Kumamoto, and at the Elemental Analysis Center, Faculty of Science, Kyushu University, Fukuoka, Japan.

Materials. Manganese(II) acetate tetrahydrate was purchased from Wako Pure Chemical Ind., Ltd. Manganese(III) acetate dihydrate, $Mn(OAc)_3 \cdot 2H_2O$, was prepared according to the method described in the literature.[20] 1,1-Diarylethenes were prepared by dehydration of the corresponding alcohols which

were synthesized from substituted acetophenones and arylmagnesium bromides. Other alkenes were purchased from Wako Pure Chemical Ind., Ltd. and used as received. 2,3-Pyrrolidinediones were prepared according to the methods described in the literature,[9] and their physical data are given below.

Ethyl 1-Benzyl-3-hydroxy-3-pyrrolin-2-one-4-carboxylate (2a): colorless prisms (ethanol-ether), mp 137°C; IR ($CHCl_3$) 3450-3000, 1710, 1690; ^1H NMR ($CDCl_3$) 8.92 (1H, s), 7.37-7.25 (5H, m), 4.68 (2H, s), 4.28 (2H, q, J = 7.33), 3.87 (2H, s), 1.3 (3H, t, J = 7.33); ^{13}C NMR ($CDCl_3$) 165.0, 163.3, 156.8, 136.1, 128.9 (2C), 128.3 (2C), 128.0, 108.0, 61.1, 47.0, 45.6, 14.2. Anal. Calcd for $C_{14}H_{15}NO_4$: C, 64.36; H, 5.79; N, 5.36. Found: C, 64.56; H, 5.84; N, 5.45.

Methyl 1-Benzyl-3-hydroxy-3-pyrrolin-2-one-4-carboxylate (2b): colorless prisms (ethanol-ether), mp 183°C; IR ($CHCl_3$) 3450-3000, 1710, 1690; ^1H NMR ($CDCl_3$) 9.00 (1H, s), 7.37-7.25 (5H, m), 4.68 (2H, s), 3.87 (2H, s), 3.81 (3H, s). Anal. Calcd for $C_{13}H_{13}NO_4$: C, 63.15; H, 5.30; N, 5.66. Found: C, 62.95; H, 5.31; N, 5.81.

Butyl 1-Butyl-3-hydroxy-3-pyrrolin-2-one-4-carboxylate (2c): colorless needles (ether), mp 124°C; IR ($CHCl_3$) 3300-2900, 1710, 1690; ^1H NMR ($CDCl_3$) 8.96 (1H, s), 4.25 (2H, t, J = 6.83), 3.97 (2H, s), 3.49 (2H, t, J = 7.32), 1.71-1.61 (2H, m), 1.60-1.45 (2H, m), 1.43-1.28 (4H, m), 0.94 (3H, t, J = 7.32), 0.92 (3H, t, J = 7.32). Anal. Calcd for $C_{13}H_{21}NO_4$: C, 61.16; H, 8.29; N, 5.49. Found: C, 61.08; H, 8.45; N, 5.68.

Ethyl 1-Butyl-3-hydroxy-3-pyrrolin-2-one-4-carboxylate (2d): colorless needles (ether), mp 64°C; IR ($CHCl_3$) 3300-2900, 1710, 1690; ^1H NMR ($CDCl_3$) 8.92 (1H, s), 4.31 (2H, q, J = 7.33), 3.97 (2H, s), 3.49 (2H, t, J = 7.32), 1.62-1.54 (2H, m), 1.35-1.30 (5H, m), 0.92 (3H, t, J = 7.33). Anal. Calcd for $C_{11}H_{17}NO_4$: C, 58.14; H, 7.54; N, 6.16. Found: C, 57.97; H, 7.72; N, 6.27.

Ethyl 1-Ethyl-3-hydroxy-3-pyrrolin-2-one-4-carboxylate (2e): colorless needles (ether), mp 91°C; IR ($CHCl_3$) 3500-2900, 1710, 1690; ^1H NMR ($CDCl_3$) 8.10 (1H, s), 4.33 (2H, q, J = 7.32), 4.0 (2H, s), 3.57 (2H, q, J = 7.33), 1.35 (3H, t, J = 7.32), 1.22 (3H, t, J = 7.33). Anal. Calcd for $C_9H_{13}NO_4$: C, 54.26; H, 6.58; N, 7.03. Found: C, 54.62; H, 6.85; N, 7.21.

Butyl 3-Hydroxy-1-methyl-3-pyrrolin-2-one-4-carboxylate (2f): colorless needles (ether), mp 98-99°C; IR ($CHCl_3$) 3300-2900, 1710, 1690; ^1H NMR ($CDCl_3$) 8.42 (1H, s), 4.24 (2H, t, J = 6.84), 3.98 (2H, s), 3.10 (3H, s), 1.71-1.64 (2H, m), 1.45-1.35 (2H, m), 0.94 (3H, t, J = 7.32). Anal. Calcd for $C_{10}H_{15}NO_4$: C, 56.33; H, 7.09; N, 6.57. Found: C, 56.52; H, 7.09; N, 6.67.

4-Cyano-1-Ethyl-3-hydroxy-3-pyrrolin-2-one (2g): colorless prisms (ethanol), mp 183-184°C; IR ($CHCl_3$) 3300-2900, 2248, 1700; ^1H NMR ($CDCl_3$) 9.65 (1H, s), 4.03 (2H, s), 3.58 (2H, q, J = 7.33), 1.24 (3H, t, J = 7.33). Anal. Calcd for $C_7H_8N_2O_2$: C, 55.26; H, 5.30; N, 18.41. Found: C, 55.12; H, 5.32; N, 18.29.

1-Butyl-4-cyano-3-hydroxy-3-pyrrolin-2-one (2h): colorless prisms (ethanol-ether), mp 138°C; IR ($CHCl_3$) 3300-2900, 2248, 1700; ^1H NMR ($CDCl_3$) 10.40 (1H, s), 4.03 (2H, s), 3.51 (2H, t, J = 7.33), 1.63-1.56 (2H, m), 1.36-1.31 (2H, m), 0.94 (3H, t, J = 7.32). Anal. Calcd for $C_9H_{12}N_2O_2$: C, 59.99; H, 6.71; N, 15.54. Found: C, 59.72; H, 6.75; N, 15.31.

1-Benzyl-4-cyano-3-hydroxy-3-pyrrolin-2-one (2i): colorless prisms (ethanol), mp 141-142°C; IR ($CHCl_3$) 3300-2900, 2248, 1710; ^1H NMR ($CDCl_3$) 7.81 (1H, s), 7.40-7.25 (5H, m), 4.67 (2H, s),

3.90 (2H, s). Anal. Calcd for $C_{12}H_{10}N_2O_2$: C, 67.28; H, 4.70; N, 13.08. Found: C, 67.60; H, 4.73; N, 13.18.

1-Benzyl-3-hydroxy-4-propionyl-3-pyrrolin-2-one (2j): colorless needles (ethanol-ether), mp 191°C; IR ($CHCl_3$) 3300-2900, 1710, 1660; ^1H NMR ($CDCl_3$) 8.40 (1H, s), 7.36-7.24 (5H, m), 4.69 (2H, s), 3.93 (2H, s), 2.80 (2H, q, J = 7.32), 1.22 (3H, t, J = 7.32). Anal. Calcd for $C_{14}H_{15}NO_3$: C, 68.56; H, 6.16; N, 5.71. Found: C, 68.43; H, 6.08; N, 5.85.

1-Benzyl-4-butyryl-3-hydroxy-3-pyrrolin-2-one (2k): colorless needles (ethanol-ether), mp 191°C; IR ($CHCl_3$) 3300-2900, 1710, 1660; ^1H NMR ($CDCl_3$) 8.40 (1H, s), 7.37-7.25 (5H, m), 4.69 (2H, s), 3.93 (2H, s), 2.70 (2H, t, J = 6.83), 1.69-1.64 (2H, m), 0.952 (3H, t, J = 7.32). Anal. Calcd for $C_{15}H_{17}NO_3$: C, 69.48; H, 6.61; N, 5.40. Found: C, 69.23; H, 6.52; N, 5.51.

1-Benzyl-3-hydroxy-4-isobutyryl-3-pyrrolin-2-one (2l): colorless needles (ethanol-ether), mp 154°C; IR ($CHCl_3$) 3300-2900, 1710, 1660; ^1H NMR ($CDCl_3$) 8.40 (1H, s), 7.36-7.26 (5H, m), 4.69 (2H, s), 3.94 (2H, s), 3.13 (1H, sept, J = 6.84), 1.13 (6H, d, J = 6.84). Anal. Calcd for $C_{15}H_{17}NO_3$: C, 69.48; H, 6.61; N, 5.40. Found: C, 69.18; H, 6.59; N, 5.40.

Manganese(III)-Based Reaction of Alkenes (1a-i) with Pyrrolidinediones (2a-l) at 23°C under a Dry Air Stream. Alkene (**1**) (1 mmol) was placed in a 50mL three-necked flask equipped with a magnetic stirrer and gas inlet tube. Glacial acetic acid (25 mL), pyrrolidinedione (**2**) (2 mmol), and manganese(III) acetate dihydrate (1-2 mmol) were added to the flask, and the mixture was stirred at 23°C under a dry air stream for the period of time shown in Table 1. The solvent was removed *in vacuo* at 45 °C within 5 min and the residue was triturated with water followed by three extractions with chloroform (30, 20 and 20 mL). The combined extracts were dried with anhydrous sodium sulfate, filtered, and concentrated to dryness. The products were separated on a silica gel column by eluting with chloroform. The molar ratios, reaction times, and product yields are summarized in Table 2. Analytical samples were further purified by recrystallization from the appropriate solvent mentioned below except for the liquid products. Physical data are given below.

8-Benzyl-6-ethoxycarbonyl-1-hydroxy-4,4-diphenyl-8-aza-2,3-dioxabicyclo[4.3.0]nonan-9-one (3aa): colorless prisms (ethanol), mp 171-172°C; IR (KBr) 3500-2900, 1730, 1707; ^1H NMR (DMSO-d_6) 8.28 (1H, s), 7.60-6.80 (15H, m), 4.54 (1H, d, J = 15.62), 4.09 (1H, d, J = 15.62), 4.00 (2H, q, J = 7.33), 3.22 (1H, d, J = 15.14), 3.18 (1H, d, J = 10.75), 3.05 (1H, d, J = 15.14), 2.92 (1H, d, J = 10.75), 1.15 (3H, t, J = 7.33); ^{13}C NMR (DMSO-d_6) 170.6, 166.4, 145.1, 142.4, 135.3, 128.3 (6C), 127.4, 126.9 (2C), 126.7 (2C), 125.7 (2C), 124.9 (2C), 100.0, 83.6, 60.9, 48.9, 47.1, 46.0, 32.1, 13.7. Anal. Calcd for $C_{28}H_{27}NO_6$: C, 71.02; H, 5.75; N, 2.96. Found: C, 70.82; H, 5.87; N, 2.91.

8-Benzyl-1-hydroxy-6-methoxycarbonyl-4,4-diphenyl-8-aza-2,3-dioxabicyclo[4.3.0]nonan-9-one (3ab): colorless needles (methanol), mp 169°C; IR (KBr) 3600-3000, 1720, 1701; ^1H NMR (DMSO-d_6) 8.28 (1H, s), 7.60-6.80 (15H, m), 4.53 (1H, d, J = 15.63), 4.10 (1H, d, J = 15.63), 3.56 (3H, s), 3.29 (1H, d, J = 15.33), 3.21 (1H, d, J = 10.75), 3.10 (1H, d, J = 15.33), 2.94 (1H, d, J = 10.75); ^{13}C NMR (DMSO-d_6) 170.6, 166.5, 145.2, 142.5, 135.2, 128.3 (4C), 128.1 (2C), 127.4, 126.9, 126.8, 126.6 (2C), 125.6 (2C), 124.8 (2C), 100.0, 84.1, 52.6, 48.9,

47.0, 45.9, 32.1. Anal. Calcd for $C_{27}H_{25}NO_6$: C, 70.58; H, 5.48; N, 3.05. Found: C, 70.49; H, 5.55; N, 3.29.

6-Butoxycarbonyl-8-butyl-1-hydroxy-4,4-diphenyl-8-aza-2,3-dioxabicyclo[4.3.0]nonan-9-one (3ac): colorless needles ($CHCl_3$), mp 146°C; IR ($CHCl_3$) 3600-3200, 1735, 1719; ^{1}H NMR ($CDCl_3$) 7.50-7.20 (10H, m), 5.20 (1H, br), 4.12 (1H, dt, J = 10.74, 6.84), 4.06 (1H, dt, J = 10.74, 6.84), 3.43 (1H, d, J = 15.14), 3.41-3.37 (1H, m), 3.1 (1H, d, J = 10.26), 3.03 (1H, d, J = 10.26), 2.96-2.93 (1H, m), 2.90 (1H, d, J = 15.14), 1.58-1.10 (8H, m), 0.90 (3H, t, J = 7.33), 0.78 (3H, t, J = 7.33); ^{13}C NMR ($CDCl_3$) 171.1, 166.3, 143.5, 142.9, 128.4 (4C), 128.0, 127.3, 126.2 (2C), 125.9 (2C), 99.4, 84.3, 65.8, 49.6, 47.2, 42.9, 33.3, 30.3, 28.6, 19.5, 19.0, 13.6, 13.5. Anal. Calcd for $C_{27}H_{33}NO_6$: C, 69.36; H, 7.11; N, 3.00. Found: C, 69.30; H, 7.23; N, 3.03.

8-Butyl-6-ethoxycarbonyl-1-hydroxy-4,4-diphenyl-8-aza-2,3-dioxabicyclo[4.3.0]nonan-9-one (3ad): colorless needles ($CHCl_3$-hexane), mp 149°C; IR ($CHCl_3$) 3590-3200, 1719, 1701; ^{1}H NMR ($CDCl_3$) 7.50-7.20 (10H, m), 5.12 (1H, s), 4.17 (1H, dq, J = 11.25, 7.33), 4.12 (1H, dq, J = 11.25, 7.33), 3.43 (1H, d, J = 15.14), 3.39-3.31 (1H, m), 3.12 (1H, d, J = 10.25), 3.03 (1H, d, J = 10.25), 3.01-2.96 (1H, m), 2.90 (1H, d, J = 15.14), 1.60-0.90 (4H, m), 1.21 (3H, t, J = 7.33), 0.78 (3H, t, J = 7.33); ^{13}C NMR ($CDCl_3$) 171.1, 166.2, 143.5, 142.3, 128.4 (4C), 128.0, 127.3, 126.2 (2C), 125.9 (2C), 99.5, 84.3, 62.0, 49.6, 47.1, 42.9, 33.4, 28.6, 19.5, 13.9, 13.6. Anal. Calcd for $C_{25}H_{29}NO_6$: C, 68.32; H, 6.65; N, 3.19. Found: C, 68.02; H, 6.80; N, 3.29.

6-Ethoxycarbonyl-8-ethyl-1-hydroxy-4,4-diphenyl-8-aza-2,3-dioxabicyclo[4.3.0]nonan-9-one (3ae): colorless needles (ethanol), mp 172°C; IR (KBr) 3600-2900, 1730, 1706; ^{1}H NMR (DMSO-d_6) 8.10 (1H, s), 7.60-7.20 (10H, m), 4.04 (2H, q, J = 7.33), 3.27 (1H, d, J = 10.74), 3.24 (1H, d, J = 15.14), 3.10 (3H, m), 2.82 (1H, d, J = 10.74), 1.12 (3H, t, J = 7.33), 0.75 (3H, t, J = 7.33); ^{13}C NMR (DMSO-d_6) 170.6, 165.3, 145.1, 142.7, 128.3 (2C), 128.1 (2C), 127.4, 126.9, 125.6 (2C), 124.9 (2C), 100.2, 83.4, 60.9, 47.5, 46.8, 36.7, 32.1, 13.7, 11.2. Anal. Calcd for $C_{23}H_{25}NO_6$: C, 67.14; H, 6.12; N, 3.40. Found: C, 67.24; H, 6.33; N, 3.26.

6-Butoxycarbonyl-1-hydroxy-8-methyl-4,4-diphenyl-8-aza-2,3-dioxabicyclo[4.3.0]nonan-9-one (3af): colorless needles ($CHCl_3$-hexane), mp 155-156°C; IR ($CHCl_3$) 3590-3200, 1726, 1706; ^{1}H NMR ($CDCl_3$) 7.50-7.20 (10H, m), 5.10 (1H, s), 4.10 (1H, dt, J = 11.24, 6.84), 4.00 (1H, dt, J = 11.24, 6.84), 3.43 (1H, d, J = 15.14), 3.15 (1H, d, J = 10.25), 3.05 (1H, d, J = 10.25), 2.88 (1H, d, J = 15.14), 2.75 (3H, s), 1.60-1.50 (2H, m), 1.35-1.22 (2H, m), 0.90 (3H, t, J = 7.33); ^{13}C NMR ($CDCl_3$) 171.1, 166.3, 143.4, 142.5, 128.5 (2C), 128.4 (2C), 128.0, 127.4, 126.1 (2C), 125.9 (2C), 99.3, 84.3, 65.9, 51.8, 47.4, 33.8, 30.3, 30.1, 19.0, 13.6. Anal. Calcd for $C_{24}H_{27}NO_6$: C, 67.75; H, 6.39; N, 4.29. Found: C, 67.72; H, 6.57; N, 4.69.

6-Cyano-8-ethyl-1-hydroxy-4,4-diphenyl-8-aza-2,3-dioxabicyclo[4.3.0]nonan-9-one (3ag): pale yellow needles ($CHCl_3$), mp 142°C; IR (KBr) 3600-2900, 2244, 1706; ^{1}H NMR ($CDCl_3$) 7.50-7.30 (10H, m), 6.20 (1H, s), 3.36 (1H, d, J = 10.26), 3.29 (1H, d, J = 14.65), 3.22 (2H, q, J = 6.80), 3.11 (1H, d, J = 10.26), 3.08 (1H, d, J = 14.65), 0.93 (3H, t, J = 6.80); ^{13}C NMR ($CDCl_3$)

165.3, 141.6, 141.5, 128.7 (2C), 128.6 (3C), 127.9, 126.1 (2C), 126.1 (2C), 119.0, 98.5, 83.9, 49.8, 39.7, 38.1, 35.7, 11.6. Anal. Calcd for $C_{21}H_{20}N_2O_4$: C, 69.22; H, 5.53; N, 7.69. Found: C, 69.04; H, 5.70; N, 7.88.

8-Butyl-6-cyano-1-hydroxy-4,4-diphenyl-8-aza-2,3-dioxabicyclo[4.3.0]nonan-9-one (3ah): pale yellow needles ($CHCl_3$), mp 132°C; IR ($CHCl_3$) 3590-3000, 2244, 1704; ^1H NMR ($CDCl_3$) 7.50-7.30 (10H, m), 6.30 (1H, s), 3.31 (1H, d, J = 10.26), 3.25 (1H, d, J = 14.65), 3.20-3.12 (2H, t, J = 6.84), 3.10 (1H, d, J = 14.65), 3.09 (1H, d, J = 10.26), 1.36-0.95 (4H, m), 0.79 (3H, t, J = 7.33); ^{13}C NMR ($CDCl_3$) 165.3, 141.6, 141.4, 128.7 (2C), 128.6 (3C), 127.8, 126.2 (2C), 126.1 (2C), 119.2, 98.3, 83.9, 50.2, 43.1, 39.7, 35.4, 28.5, 19.4, 13.5. Anal. Calcd for $C_{23}H_{24}N_2O_4$: C, 70.39; H, 6.16; N, 7.14. Found: C, 70.60; H, 6.36; N, 7.28.

8-Benzyl-6-cyano-1-hydroxy-4,4-diphenyl-8-aza-2,3-dioxabicyclo[4.3.0]nonan-9-one (3ai): colorless needles (ethanol), mp 158°C; IR (KBr) 3600-2900, 2244, 1710; ^1H NMR (DMSO-d_6) 9.06 (1H, s), 7.43-6.98 (15H, m), 4.49 (1H, d, J = 15.14), 4.32 (1H, d, J = 15.14), 3.47 (1H, d, J = 10.25), 3.34 (1H, d, J = 14.65), 3.23 (1H, d, J = 14.65), 3.14 (1H, d, J = 10.25); ^{13}C NMR (DMSO-d_6) 164.9, 142.8, 141.8, 134.9, 128.5 (2C), 128.3, (2C) 128.2 (2C), 127.8, 127.4 (2C), 127.0 (2C), 125.5 (2C), 125.2 (2C), 119.0, 99.1, 83.5, 49.6, 45.6, 42.9, 35.6. Anal. Calcd for $C_{26}H_{22}N_2O_4$: C, 73.22; H, 5.20; N, 6.57. Found: C, 73.26; H, 5.20; N, 6.79.

8-Benzyl-1-hydroxy-6-propionyl-4,4-diphenyl-8-aza-2,3-dioxabicyclo[4.3.0]nonan-9-one (3aj): colorless needles ($CHCl_3$), mp 178°C; IR (KBr) 3600-3000, 1730, 1706; ^1H NMR (DMSO-d_6) 8.34 (1H, s), 7.47-6.83 (15H, m), 4.68 (1H, d, J = 15.13), 4.09 (1H, d, J = 15.13), 3.19 (1H, d, J = 11.23), 3.12 (1H, d, J = 14.65), 3.02 (1H, d, J = 14.65), 2.91 (1H, d, J = 11.23), 2.52 (1H, dt, J = 10.75, 7.32), 2.32 (1H, dt, J = 10.75, 7.32), 0.88 (3H, t, J = 7.32); ^{13}C NMR (DMSO-d_6) 206.7, 166.8, 142.5, 135.0, 132.6, 128.5, 128.4 (2C), 128.3 (2C), 128.2 (2C), 127.3, 126.9 (2C), 126.6 (2C), 125.4, 124.9 (2C), 100.2, 83.9, 51.2, 47.9, 45.7, 38.8, 31.0, 7.7. Anal. Calcd for $C_{28}H_{27}NO_5$: C, 73.50; H, 5.95; N, 3.06. Found: C, 73.33; H, 5.98; N, 3.17.

8-Benzyl-6-butyryl-1-hydroxy-4,4-diphenyl-8-aza-2,3-dioxabicyclo[4.3.0]nonan-9-one (3ak): colorless needles ($CHCl_3$), mp 150°C; IR (KBr) 3600-3000, 1730, 1704; ^1H NMR (DMSO-d_6) 8.33 (1H, s), 7.50-6.84 (15H, m), 4.62 (1H, d, J = 15.14), 4.13 (1H, d, J = 15.14), 3.18 (1H, d, J = 10.25), 3.12 (1H, d, J = 15.14), 3.00 (1H, d, J = 15.14), 2.93 (1H, d, J = 10.25), 2.42 (1H, dt, J = 10.75, 6.7), 2.29 (1H, dt, J = 10.75, 6.7), 1.43 (2H, m), 0.77 (3H, t, J = 7.3); ^{13}C NMR (DMSO-d_6) 205.9, 164.8, 145.6, 142.6, 135.0, 128.4 (2C), 128.3 (2C), 128.2 (2C), 127.3, 127.0, 126.9, 126.8, 125.4, 124.9 (4C), 100.2, 83.9, 51.1, 47.9, 45.7, 39.7, 32.0, 16.4, 13.3. Anal. Calcd for $C_{29}H_{29}NO_5$: C, 73.87; H, 6.20; N, 2.97. Found: C, 73.99; H, 6.18; N, 3.09.

8-Benzyl-1-hydroxy-6-isobutyryl-4,4-diphenyl-8-aza-2,3-dioxabicyclo[4.3.0]nonan-9-one (3al): colorless needles ($CHCl_3$), mp 156°C; IR (KBr) 3600-3200, 1730, 1704; ^1H NMR (DMSO-d_6) 8.41 (1H, s), 7.51-6.85 (15H, m), 4.59 (1H, d, J = 15.14), 4.12 (1H, d, J = 15.14), 3.30 (1H, d, J = 15.14), 3.21 (1H, d, J = 11.23), 3.00 (1H, d, J = 15.14), 2.93 (1H, d, J = 11.23), 2.88 (1H, sept, J = 6.35), 0.97 (3H, d, J = 6.35), 0.93 (3H, d, J = 6.35); ^{13}C NMR (DMSO-d_6) 211.0, 166.6, 145.6, 142.5, 135.1, 128.4 (2C), 128.3 (2C), 128.2 (2C), 127.3, 127.0, 126.9, 126.7, 125.4, 124.8 (4C),

100.2, 83.6, 52.1, 47.5, 45.8, 36.0, 32.0, 20.4, 19.9. Anal. Calcd for $C_{29}H_{29}NO_5$: C, 73.87; H, 6.20; N, 2.97. Found: C, 73.97; H, 6.34; N, 2.63.

8-Benzyl-6-ethoxycarbonyl-1-hydroxy-4,4-bis(4-methylphenyl)-8-aza-2,3-dioxabicyclo[4.3.0]nonan-9-one (3ba): colorless needles (ethanol), mp 160°C; IR (KBr) 3600-3200, 1720, 1710; ^{1}H NMR (DMSO-d_6) 8.18 (1H, s), 7.40-6.80 (13H, m), 4.60 (1H, d, J =16.11), 4.04 (2H, q, J = 7.32), 3.99 (1H, d, J = 16.11), 3.15 (1H, d, J = 15.14), 3.09 (1H, d, J = 10.74), 3.02 (1H, d, J = 15.14), 2.93 (1H, d, J = 10.74), 2.23 (6H, s), 1.15 (3H, t, J = 7.32); ^{13}C NMR (DMSO-d_6) 170.7, 166.3, 142.2, 139.5, 136.7, 135.9, 135.2, 128.7 (4C), 128.2 (2C), 126.7, 126.6 (2C), 125.6 (2C), 125.0 (2C), 99.9, 83.5, 60.8, 48.8, 47.0, 45.8, 31.6, 20.4 (2C), 13.6. Anal. Calcd for $C_{30}H_{31}NO_6$: C, 71.84; H, 6.23; N, 2.79. Found: C, 72.11; H, 6.22; N, 2.78.

8-Benzyl-6-ethoxycarbonyl-1-hydroxy-4,4-bis(4-methoxyphenyl)-8-aza-2,3-dioxabicyclo[4.3.0]nonan-9-one (3ca): colorless needles (ethanol), mp 176°C; IR (KBr) 3600-2900, 1730, 1710; ^{1}H NMR (DMSO-d_6) 8.18 (1H, s), 7.50-6.70 (13H, m), 4.60 (1H, d, J = 15.63), 4.07-3.99 (3H, m), 3.72 (3H, s), 3.70 (3H, s), 3.12 (1H, d, J = 10.74), 3.06-2.90 (2H, m), 2.96 (1H, d, J = 10.74),1.10 (3H, t, J = 7.33); ^{13}C NMR (DMSO-d_6) 170.7, 166.3, 158.5, 157.9, 138.0, 135.2, 134.2, 128.2 (2C), 127.1, 126.7 (4C), 126.7 (2C), 113.5 (4C), 99.7, 83.3, 60.8, 48.8, 45.8, 31.7, 55.0, 54.9, 46.9, 13.6. Anal. Calcd for $C_{30}H_{31}NO_8$: C, 67.53; H, 5.86; N, 2.63. Found: C, 67.44; H, 5.78; N, 2.60.

8-Benzyl-4,4-bis(4-chlorophenyl)-6-ethoxycarbonyl-1-hydroxy-8-aza-2,3-dioxabicyclo[4.3.0]nonan-9-one (3da): colorless needles (ethanol), mp 149°C; IR (KBr) 3600-3000, 1732, 1706; ^{1}H NMR (DMSO-d_6) 8.36 (1H, s), 7.60-6.80 (13H, m), 4.64 (1H, d, J = 15.80), 4.12 (2H, q, J = 7.33), 3.96 (1H, d, J = 15.80), 3.25 (1H, d, J = 14.65), 3.18 (1H, d, J = 10.75), 3.0 (1H, d, J = 14.65), 2.8 (1H, d, J = 10.75), 1.11 (3H, t, J = 7.33); ^{13}C NMR (DMSO-d_6) 170.4, 165.8, 143.3, 140.8, 135.1, 132.4, 132.0, 128.5 (2C), 128.4 (2C), 128.3 (4C), 127.6, 126.9 (2C), 126.6 (2C), 99.8, 82.9, 61.0, 48.6, 46.7, 45.7, 31.5, 13.6. Anal. Calcd for $C_{28}H_{25}NO_6Cl_2$: C, 62.00; H, 4.65; N, 2.58. Found: C, 61.73; H, 4.62; N, 2.74.

8-Benzyl-6-ethoxycarbonyl-4,4-bis(4-fluorophenyl)-1-hydroxy-8-aza-2,3-dioxabicyclo[4.3.0]nonan-9-one (3ea): colorless needles (ethanol), mp 154°C; IR (KBr) 3600-2900, 1740, 1708; ^{1}H NMR (DMSO-d_6) 8.28 (1H, s), 7.36-6.82 (13H, m), 4.62 (1H, d, J = 15.13), 4.05 (2H, q, J = 7.32), 4.01 (1H, d, J = 15.13), 3.20 (1H, d, J = 15.14), 3.17 (1H, d, J = 10.74), 3.00 (1H, d, J = 15.14), 2.82 (1H, d, J = 10.74), 1.11 (3H, t, J = 7.32); ^{13}C NMR (DMSO-d_6) 170.5, 166.2, 166.0, 155.8, 138.2, 138.1, 135.2, 128.2 (2C), 128.1, 127.7, 127.5, 127.1, 126.9, 126.8 (2C), 115.7, 115.5, 114.7 (2C), 99.9, 83.5, 60.9, 48.6, 46.8, 45.8, 31.9, 13.6. Anal. Calcd for $C_{28}H_{25}NO_6F_2$: C, 66.00; H, 4.99; N, 2.73. Found: C, 66.19; H, 4.99; N, 2.75.

8-Benzyl-6-ethoxycarbonyl-1-hydroxy-4-methyl-4-phenyl-8-aza-2,3-dioxabicyclo[4.3.0]nonan-9-one (3fa): colorless needles ($CHCl_3$-hexane), mp 170°C; IR ($CHCl_3$) 3600-3000, 1740, 1720; ^{1}H NMR ($CDCl_3$) 7.34-7.21 (10H, m), 5.25 (1H, s), 4.63 (1H, d, J = 15.14), 4.48 (1H, d, J = 15.14), 3.91 (1H, dq, J = 10.74, 7.33), 3.72 (1H, dq, J = 10.74, 7.33), 3.51 (1H, d, J = 10.74), 3.30 (1H, d, J = 10.74), 3.10 (1H, d, J = 14.65), 2.11 (1H, d, J = 14.65), 1.50 (3H, s), 1.00

(3H, t, J = 7.33); ^{13}C NMR ($CDCl_3$) 171.6, 167.0, 144.5, 134.9, 128.8 (2C), 128.4 (2C), 128.2 (2C), 128.0, 127.2, 124.5 (2C), 101.1, 81.1, 61.9, 50.7, 47.0, 45.7, 38.9, 28.6, 13.5. Anal. Calcd for $C_{23}H_{25}NO_6$: C, 67.14; H, 6.12; N, 3.40. Found: C, 67.29; H, 6.026; N, 3.40.

8-Benzyl-6-ethoxycarbonyl-1-hydroxy-4,4-dimethyl-8-aza-2,3-dioxabicyclo[4.3.0]nonan-9-one (3ga): colorless needles ($CHCl_3$-hexane), mp 55-56°C; IR ($CHCl_3$) 3600-3000, 1732, 1716; ^{1}H NMR ($CDCl_3$) 7.36-7.27 (5H, m), 5.42 (1H, s), 4.63 (1H, d, J = 14.65), 4.45 (1H, d, J = 14.65), 4.17 (1H, dq, J = 10.74, 7.33), 4.09(1H, dq, J = 10.74, 7.33), 3.43 (1H, d, J = 10.74), 3.29 (1H, d, J = 10.74), 2.55 (1H, d, J = 14.65), 1.64 (1H, d, J = 14.65), 1.31 (3H, s), 1.30 (3H, s), 1.18 (3H, t, J = 7.33); ^{13}C NMR ($CDCl_3$) 171.2, 167.0, 134.6, 128.5 (2C), 128.1 (2C), 127.7, 99.5, 77.0, 61.6, 50.8, 46.9, 45.1, 36.0, 27.6, 25.5, 13.6. Anal. Calcd for $C_{18}H_{23}NO_6$: C, 61.88; H, 6.64; N, 4.01. Found: C, 61.68; H, 6.56; N, 4.02.

8-Benzyl-6-ethoxycarbonyl-4,4-diethyl-1-hydroxy-8-aza-2,3-dioxabicyclo[4.3.0]nonan-9-one (3ha): colorless microcrystals (CH_2Cl_2-hexane), mp 124°C; IR ($CHCl_3$) 3600-3000, 1736, 1710; ^{1}H NMR ($CDCl_3$) 7.36-7.26 (5H, m), 5.42 (1H, s), 4.60 (1H, d, J = 14.65), 4.47 (1H, d, J = 14.65), 4.17 (1H, dq, J = 10.74, 7.33), 4.10 (1H, dq, J = 10.74, 7.33), 3.43 (1H, d, J = 10.74), 3.21 (1H, d, J = 10.74), 2.47 (1H, d, J = 14.65), 1.83-1.61 (2H, m), 1.60 (1H, d, J = 14.65), 1.42 (2H, q, J = 7.33), 1.19 (3H, t, J = 7.33), 0.86 (3H, t, J = 7.33), 0.82 (3H, t, J = 7.33); ^{13}C NMR ($CDCl_3$) 172.0, 167.1, 134.8, 128.8 (2C), 128.4 (2C), 128.0, 100.1, 82.0, 62.0, 51.5, 47.1, 45.7, 34.1, 27.5, 26.6, 13.8, 7.5, 7.2. Anal. Calcd for $C_{20}H_{27}NO_6$: C, 63.64; H, 7.21; N, 3.71. Found: C, 63.70; H, 7.12; N, 3.88.

14-Benzyl-12-ethoxycarbonyl-1-hydroxy-14-aza-2,3-dioxatricyclo[10.3.0.0^{4,11}]pentadecan-15-one (3ia): colorless needles (CH_2Cl_2-hexane), mp 171°C; IR ($CHCl_3$) 3600-3000, 1735, 1707; ^{1}H NMR ($CDCl_3$) 7.36-7.20 (5H, m), 5.10 (1H, s), 4.65 (1H, d, J = 14.65), 4.44 (1H, d, J = 14.65), 4.17 (1H, dq, J = 10.74, 7.33), 4.09 (1H, dq, J = 10.74, 7.33), 4.00 (1H, m), 3.37 (1H, d, J = 10.74), 3.31 (1H, d, J = 10.74), 2.86 (1H, m), 1.90-1.20 (12H, m), 1.18 (3H, t, J = 7.33); ^{13}C NMR ($CDCl_3$) 170.4, 166.8, 134.8, 128.7 (2C), 128.4 (2C), 127.9, 100.1, 81.7, 61.8, 53.2, 47.5, 46.9, 37.4, 29.4, 26.7, 26.0, 25.7, 24.8, 22.8, 13.9. Anal. Calcd for $C_{22}H_{29}NO_6$: C, 65.49; H, 7.24; N, 3.47. Found: C, 65.70; H, 7.40; N, 3.62.

1-Benzyl-4-ethoxycarbonyl-4-[2-(4-methoxyphenyl)-2-oxoethyl]-2,3-pyrrolidinedione (4): pale yellow liquid; IR ($CHCl_3$) 1775, 1740, 1718; ^{1}H NMR ($CDCl_3$) 7.87 (2H, m), 7.20-7.40 (5H, m), 6.91 (2H, m), 4.94 (1H, d, J = 14.65), 4.58 (1H, d, J = 14.65), 4.10 (2H, J = 7.32), 4.02 (1H, d, J = 11.23), 3.95 (1H, d, J = 18.56), 3.85 (3H, s), 3.74 (1H, d, J = 18.56), 3.37 (1H, d, J = 11.23), 1.13 (3H, t, J = 7.32); ^{13}C NMR ($CDCl_3$) 194.4, 194.2, 167.0, 164.1, 158.2, 134.2, 130.5 (2C), 128.7 (2C), 128.3 (2C), 128.1, 128.0, 113.8 (2C), 62.6, 55.4, 50.4, 48.3, 43.6, 13.6, 51.4. Anal. Calcd for $C_{23}H_{23}NO_6$: C, 67.47; H, 5.66; N, 3.42. Found: C, 67.66; H, 5.75; N, 3.49.

Manganese(III)-Based Reaction of 1,1-Diaylethenes (1a-e) with Ethyl 1-Benzyl-3-hydroxy-3-pyrrolin-2-one-4-carboxylate (2a) at Elevated Temperature. A general procedure is as follows. 1,1-Diarylethene (**1**) (1 mmol) was placed in a 50mL flask equipped with a magnetic stirrer. Glacial acetic acid (15 mL), and **2a** (2 mmol) were added. The mixture was heated at the

temperature shown in Table 2 and then manganese(III) acetate (3 mmol) was added. The mixture was stirred until the dark-brown of Mn(III) disappeared. The solvent was removed *in vacuo* and the residue was triturated with water followed by extraction with chloroform. The extract was dried over anhydrous sodium sulfate, filtered and concentrated to dryness. The products were separated on silica gel TLC (Wakogel B-10 or Merck Kieselgel $60F_{254}$) with 1% MeOH-CH_2Cl_2 as the developing solvent. Analytical samples were further purified by recrystallization from the appropriate solvent mentioned below.

1-Benzyl-4-ethoxycarbonyl-4-(2,2-diphenyl)ethenyl-2,3-pyrrolidinedione (6aa): colorless needles (CH_2Cl_2-hexane), mp 84°C; IR ($CHCl_3$) 1770, 1740, 1710; ^1H NMR ($CDCl_3$) 7.34-6.96 (15H, m), 6.62 (1H, s), 4.56 (1H, d, J = 14.16), 4.22 (1H, d, J = 14.16), 4.14 (1H, dq, J = 10.74, 7.33), 4.08 (1H, dq, J = 10.74, 7.33), 3.50 (1H, d, J = 11.23), 3.17 (1H, d, J = 11.23), 1.16 (3H, t, J = 7.33); ^{13}C NMR ($CDCl_3$) 193.8, 167.1, 157.1, 146.3, 141.0, 138.7, 133.8, 129.4 (2C), 128.9 (2C), 128.7 (2C), 128.6 (2C), 128.5 (2C), 128.4 (2C), 128.3, 127.4 (2C), 123.2, 63.1, 56.8, 50.8, 48.5, 13.8. Anal. Calcd for $C_{28}H_{25}NO_4$: C, 76.52; H, 5.73; N, 3.19. Found: C, 76.67; H, 5.77; N, 3.24.

1-Benzyl-4-ethoxycarbonyl-4-[2,2-bis(4-methylphenyl)]ethenyl-2,3-pyrrolidinedione (6ba): colorless needles (CH_2Cl_2-hexane), mp 149°C; IR ($CHCl_3$) 1773, 1740, 1710; ^1H NMR ($CDCl_3$) 7.28-6.85 (13H, m), 6.56 (1H, s), 4.58 (1H, d, J = 14.16), 4.20 (1H, d, J = 14.16), 4.14 (1H, dq, J = 10.74, 7.33), 4.08 (1H, dq, J = 10.74, 7.33), 3.52 (1H, d, J = 11.23), 3.21 (1H, d, J = 11.23), 2.37 (3H, s), 2.27 (3H, s), 1.16 (3H, t, J = 7.33); ^{13}C NMR ($CDCl_3$) 194.1, 167.2, 157.2, 146.0, 138.4, 138.0 (2C), 135.8, 133.8, 129.3 (2C), 129.2 (2C), 128.9 (2C), 128.7 (2C), 128.5 (2C), 128.2, 127.2 (2C), 122.1, 63.0, 56.8, 50.9, 48.3, 21.2, 21.0, 13.8. Anal. Calcd for $C_{30}H_{29}NO_4$: C, 77.05; H, 6.25; N, 2.30. Found: C, 76.65; H, 6.42; N, 2.99.

1-Benzyl-4-ethoxycarbonyl-4-[2,2-bis(4-methoxyphenyl)]ethenyl-2,3-pyrrolidinedione (6ca): colorless needles (CH_2Cl_2-hexane), mp 119°C; IR ($CHCl_3$) 1771, 1740, 1710; ^1H NMR ($CDCl_3$) 7.31-6.76 (13H, m), 6.47 (1H, s), 4.59 (1H, d, J = 14.65), 4.26 (1H, d, J = 14.65), 4.16 (1H, dq, J = 10.74, 7.33), 4.08 (1H, dq, J = 10.74, 7.33), 3.83 (3H, s), 3.75 (3H, s), 3.54 (1H, d, J = 11.23), 3.21 (1H, d, J = 11.23), 1.15 (3H, t, J = 7.33); ^{13}C NMR ($CDCl_3$) 194.2, 167.2, 157.2, 159.7, 159.5, 145.4, 133.9, 133.8, 131.0, 130.6 (2C), 128.8 (2C), 128.7 (2C), 128.5 (2C), 128.2, 121.1, 114.0 (2C), 113.6 (2C), 63.0, 56.9, 55.3, 55.2, 51.0, 48.4, 13.8. Anal. Calcd for $C_{30}H_{29}NO_6$: C, 72.13; H, 5.85; N, 2.80. Found: C, 72.23; H, 5.87; N, 2.97.

1-Benzyl-4-ethoxycarbonyl-4-[2,2-bis(4-fluorophenyl)]ethenyl-2,3-pyrrolidinedione (6ea): colorless microcrystals (CH_2Cl_2-hexane), mp 102-103°C; IR ($CHCl_3$) 1776, 1740, 1710; ^1H NMR ($CDCl_3$) 7.32-6.94 (13H, m), 6.52 (1H, s), 4.54 (1H, d, J = 14.64), 4.39 (1H, d, J = 14.64), 4.17 (1H, dq, J = 10.74, 7.32), 4.08 (1H, dq, J = 10.74, 7.32), 3.54 (1H, d, J = 11.23), 3.16 (1H, d, J = 11.23), 1.15 (3H, t, J = 7.32); ^{13}C NMR ($CDCl_3$) 193.7, 166.9, 164.1, 163.8, 161.6, 161.3, 157.0, 144.3, 137.1, 134.4, 133.7, 131.2, 131.4, 129.2, 129.1, 128.9 (2C), 128.7 (2C), 128.4, 123.3, 115.9, 115.7, 115.4, 115.2, 63.3, 56.9, 50.8, 48.5, 13.8. Anal. Calcd for $C_{28}H_{23}NO_4F_2$: C, 70.73; H, 4.87; N, 2.95. Found: C, 70.78; H, 5.02; N, 2.98.

4-(2-Acetoxy-2,2-diphenyl)ethyl-1-benzyl-4-ethoxycarbonyl-2,3-pyrrolidinedione (7aa): colorless plates (CH_2Cl_2-hexane), mp 84 °C; IR ($CHCl_3$) 1773, 1760, 1745, 1714; ^1H NMR ($CDCl_3$) 7.34-7.14 (15H, m), 4.64 (1H, d, J = 14.16), 4.22 (1H, d, J = 14.16), 3.98 (1H, dq, J = 10.74, 7.32), 3.82 (1H, dq, J = 10.74, 7.32), 3.62 (1H, d, J = 15.14), 3.56 (1H, d, J = 15.14), 3.51 (1H, d, J = 11.23), 2.77 (1H, d, J = 11.23), 1.96 (3H, s), 1.09 (3H, t, J = 7.32); ^{13}C NMR ($CDCl_3$) 194.0, 168.3, 166.9, 157.5, 143.8, 142.7, 133.8, 128.8 (2C), 128.5 (2C), 128.2 (3C), 128.1 (2C), 127.4 (2C), 126.0 (2C), 125.8 (2C), 84.1, 62.6, 53.8, 48.3, 47.3, 40.2, 21.9, 13.4. Anal. Calcd for $C_{30}H_{29}NO_6$: C, 72.13; H, 5.85; N, 2.80. Found: C, 72.38; H, 5.72; N, 2.93.

4-[2-Acetoxy-2,2-bis(4-chlorophenyl)]ethyl-1-benzyl-4-ethoxycarbonyl-2,3-pyrrolidinedione (7da): colorless plates (CH_2Cl_2-hexane), mp 102-103 °C; IR ($CHCl_3$) 1774, 1760, 1742, 1716; ^1H NMR ($CDCl_3$) 7.36-7.09 (13H, m), 4.54 (1H, d, J = 14.16), 4.42 (1H, d, J = 14.16), 4.00 (1H, dq, J = 10.74, 7.32), 3.81 (1H, dq, J = 10.74, 7.32), 3.62 (1H, d, J = 15.14), 3.55 (1H, d, J = 11.23), 3.41 (1H, d, J = 15.14), 2.75 (1H, d, J = 11.23), 1.95 (3H, s), 1.10 (3H, t, J = 7.32); ^{13}C NMR ($CDCl_3$) 193.8, 168.3, 166.5, 157.4, 142.1, 141.0, 133.8 (2C), 133.7, 129.0 (2C), 128.7 (2C), 128.6 (3C), 128.5 (2C), 127.6 (2C), 127.4 (2C), 83.4, 63.0, 54.1, 48.6, 47.5, 40.0, 22.0, 13.6. Anal. Calcd for $C_{30}H_{27}NO_6Cl_2$: C, 63.39; H, 4.79; N, 2.46. Found: C, 63.12; H, 4.98; N, .2.66.

4-[2-Acetoxy-2,2-bis(4-fluorophenyl)]ethyl-1-benzyl-4-ethoxycarbonyl-2,3-pyrrolidinedione (7ea): colorless plates (CH_2Cl_2-hexane), mp 168 °C; IR ($CHCl_3$) 1776, 1760, 1742, 1710; ^1H NMR ($CDCl_3$) 7.36-6.90 (13H, m), 4.52 (1H, d, J = 14.1), 4.46 (1H, d, J = 14.16), 4.01 (1H, dq, J = 10.74, 7.32), 3.83 (1H, dq, J = 10.74, 7.32), 3.63 (1H, d, J = 15.14), 3.56 (1H, d, J = 11.23), 3.42 (1H, d, J = 15.14), 2.76 (1H, d, J = 11.23), 1.93 (3H, s), 1.11 (3H, t, J = 7.32); ^{13}C NMR ($CDCl_3$) 193.8, 168.4, 167.4, 166.7, 157.4, 156.4, 139.6, 139.4, 138.7, 138.5, 133.8, 129.0 (2C), 128.7 (2C), 128.5, 128.4, 128.2, 128.0, 127.8, 115.8, 115.7, 114.9, 114.7, 83.7, 63.0, 54.2, 48.6, 47.5, 40.6, 22.1, 13.6. Anal. Calcd for $C_{30}H_{27}NO_6F_2$: C, 67.28; H, 4.13; N, 2.61. Found: C, 67.37; H, 4.11; N, .2.75.

Acid-Catalyzed Decomposition of 3aa and 3ai. A solution of **3aa** (100 mg) in acetic acid (10 mL) was heated under reflux for 3 h. After removing the acetic acid, the mixture was separated on a silica gel TLC developed with chloroform to give 2-ethoxycarbonyl-4,4-diphenylbutanolide (**8a**; 46.5 mg, 71% yield). A similar reaction of **3ai** (112 mg) gave **8i** (25 mg, 40% yield).

2-Ethoxycarbonyl-4,4-diphenylbutanolide (8a): colorless prisms (benzene-hexane), mp 67 °C (lit.,[21] mp 67.4-68.5 °C); IR ($CHCl_3$) 1782, 1735; ^1H NMR ($CDCl_3$) 7.43-7.26 (10H, m), 4.20 (2H, q, J = 7.33), 3.61 (1H, dd, J = 9.27, 10.26), 3.28-3.25 (2H, m), 1.25 (3H, t, J = 7.33); ^{13}C NMR ($CDCl_3$) 170.9, 167.2, 142.6, 141.9, 128.8 (2C), 128.6 (2C), 128.2, 128.1, 125.5 (2C), 125.3 (2C), 88.4, 62.2, 47.1, 39.4, 14.0; MS *m/z* (rel intensity), 310 (M^+, 20), 183 (100), 105 (69), 77 (36), 55 (54).

2-Cyano-4,4-diphenylbutanolide (8i): colorless needles ($CHCl_3$-hexane), mp 123 °C (lit.,[22] mp 123-124 °C); IR ($CHCl_3$) 2224, 1785; ^1H NMR ($CDCl_3$) 7.40-7.25 (10H, m), 3.66 (1H, dd, J = 12.21, 7.81), 3.46 (1H, dd, J = 12.7, 7.81), 3.13 (1H, dd, J = 12.7, 12.21); MS *m/z* (rel intensity), 263 (M^+, 58), 186 (36), 183 (35), 105 (100), 77 (54), 51 (30).

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