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

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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...
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. Recently, it was reported that the pyrrolidinedione derivatives were synthesized as endothelin receptor antagonists. 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-1). The pyrrolidinediones (2a-f) were prepared by treatment of alkyl (β-alkylamino)propionates 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. 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. 4-Acyl-2,3-pyrrolidinediones (2j-1) were prepared from methyl acylpyruvates and methyldenebenzylamine resulted from the normal procedure for the preparation of aldimines. 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

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

$^a$ The reaction was carried out under bubbling dry air.  
$^b$ 1:2:1: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
Table 2. Reaction of Alkenes (la-e) with Ethyl 1-Benzyl-2,3-pyrrolidinedione-4-carboxylate (2a) in the Presence of Manganese(III) Acetate at Elevated Temperaturea

<table>
<thead>
<tr>
<th>Entry</th>
<th>Alkene</th>
<th>Temperature (°C)</th>
<th>Time (min)</th>
<th>Product (Yield%)b</th>
</tr>
</thead>
<tbody>
<tr>
<td>21c</td>
<td>la</td>
<td>70</td>
<td>10</td>
<td>6aa (18)</td>
</tr>
<tr>
<td>22</td>
<td>la</td>
<td>70</td>
<td>30</td>
<td>6aa (21)</td>
</tr>
<tr>
<td>23</td>
<td>la</td>
<td>reflux</td>
<td>2</td>
<td>6aa (50)</td>
</tr>
<tr>
<td>24</td>
<td>lb</td>
<td>70</td>
<td>16</td>
<td>6ba (62)</td>
</tr>
<tr>
<td>25</td>
<td>lb</td>
<td>reflux</td>
<td>2</td>
<td>6ba (79)</td>
</tr>
<tr>
<td>26</td>
<td>lc</td>
<td>70</td>
<td>12</td>
<td>6ca (87)</td>
</tr>
<tr>
<td>27</td>
<td>lc</td>
<td>reflux</td>
<td>1</td>
<td>6ca (90)</td>
</tr>
<tr>
<td>28</td>
<td>ld</td>
<td>70</td>
<td>40</td>
<td>7da (66)</td>
</tr>
<tr>
<td>29</td>
<td>ld</td>
<td>reflux</td>
<td>2</td>
<td>7da (64)</td>
</tr>
<tr>
<td>30</td>
<td>le</td>
<td>70</td>
<td>40</td>
<td>7ea (45)</td>
</tr>
<tr>
<td>31</td>
<td>le</td>
<td>reflux</td>
<td>2</td>
<td>6ea (43)</td>
</tr>
</tbody>
</table>

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 (la-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 la afforded both 6 and 7 in moderate yields, only 6 was obtained in good yield in a similar reaction of lb, 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 le 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%). 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).
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. 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. After the one-electron transfer oxidation step to form radical B, the reaction pathway could depend on the ambient temperature. At 23 °C, radical B could trap molecular oxygen to produce peroxyl radical D, which would be easily reduced with manganese(II) and cyclized to give 1,2-dioxan-3-ol. 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. From C, a β-proton elimination and an attack of an acetate ion would yield 6 and 7, respectively.
The acid-catalyzed decomposition of 3ca to give ketone (4) and phenol (5) (Entry 3) could be responsible for the aryl migration as shown in Scheme 5. 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. 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 13C 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)₃·2H₂O, was prepared according to the method described in the literature. 1,1-Diaryl alkenes 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, 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 (CHCl₃) 3450-3000, 1710, 1690; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₁₄H₁₅NO₄: 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 (CHCl₃) 3450-3000, 1710, 1690; ¹H NMR (CDCl₃) 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 C₁₃H₁₃NO₄: 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 (CHCl₃) 3300-2900, 1710, 1690; ¹H NMR (CDCl₃) 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 C₁₃H₂₁NO₄: 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 (CHCl₃) 3300-2900, 1710, 1690; ¹H NMR (CDCl₃) 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 C₁₁H₁₇NO₄: C, 58.14; H, 7.54; N, 6.16. Found: C, 57.97; H, 7.72; N, 6.27.

**Ethyl 1-Butyl-3-hydroxy-3-pyrrolin-2-one-4-carboxylate (2e):** colorless needles (ether), mp 91°C; IR (CHCl₃) 3500-2900, 1710, 1690; ¹H NMR (CDCl₃) 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 C₉H₁₃NO₄: 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 (CHCl₃) 3300-2900, 1710, 1690; ¹H NMR (CDCl₃) 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 C₁₀H₁₅NO₄: 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 (CHCl₃) 3300-2900, 2248, 1700; ¹H NMR (CDCl₃) 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 C₇H₈N₂O₂: C, 55.26; H, 5.30; N, 18.41. Found: C, 55.12; H, 5.32; N, 18.29.

**1-Benzyl-4-cyano-3-hydroxy-3-pyrrolin-2-one (2h):** colorless prisms (ethanol-ether), mp 138°C; IR (CHCl₃) 3300-2900, 2248, 1700; ¹H NMR (CDCl₃) 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 C₉H₁₂N₂O₂: C, 59.99; H, 6.71; N, 15.54. Found: C, 59.72; H, 6.75; N, 15.31.
3.90 (2H, s). Anal. Calcd for C_{12}H_{10}N_{2}O_{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 (CHCl₃) 3300-2900, 1710, 1660; ¹H NMR (CDCl₃) 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-butyl-3-hydroxy-3-pyrrolin-2-one (2k): colorless needles (ethanol-ether), mp 191°C; IR (CHCl₃) 3300-2900, 1710, 1660; ¹H NMR (CDCl₃) 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, 69.23; 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 (CHCl₃) 3300-2900, 1710, 1660; ¹H NMR (CDCl₃) 8.40 (1H, s), 7.36-7.25 (5H, m), 4.69 (2H, s), 3.18 (IH, d, J = 7.33), 3.16 (6H, d, J = 7.33). 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-d₆) 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); ¹³C NMR (DMSO-d₆) 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-d₆) 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); ¹³C NMR (DMSO-d₆) 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,
6-Butoxycarbonyl-8-butyl-1-hydroxy-4,4-diphenyl-8-aza-2,3-dioxabicyclo[4.3.0]nonan-9-one (3ac): colorless needles (CHCl₃), mp 146°C; IR (CHCl₃) 3600-3200, 1735, 1719; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₂₇H₂₅NO₆: C, 70.58; H, 5.48; N, 3.05. Found: C, 70.49; H, 5.55; N, 3.29.

8-Butyl-6-ethoxycarbonyl-1-hydroxy-4,4-diphenyl-8-aza-2,3-dioxabicyclo[4.3.0]nonan-9-one (3ad): colorless needles (CHCl₃-hexane), mp 149°C; IR (CHCl₃) 3590-3200, 1719, 1701; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₂₅H₂₉NO₆: 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; ¹H NMR (DMSO-d₆) 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); ¹³C NMR (DMSO-d₆) 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 C₂₃H₂₅NO₆: 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 (CHCl₃-hexane), mp 155-156°C; IR (CHCl₃) 3590-3200, 1726, 1706; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₂₄H₂₇NO₆: 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 (CHCl₃), mp 142°C; IR (KBr) 3600-2900, 2244, 1706; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃)
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_{2}O_{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 (CHCl₃), mp 132°C; IR (CHCl₃) 3590-3000, 2244, 1704; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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_{2}O_{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-d₆) 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); ¹³C NMR (DMSO-d₆) 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_{2}O_{4}: C, 73.22; H, 5.20; N, 6.57. Found: C, 73.26; H, 5.20; N, 6.79.

8-Benzyl-1-hydroxy-4-propionyl-4,4-diphenyl-8-aza-2,3-dioxabicyclo[4.3.0]nonan-9-one (3aj): colorless needles (CHCl₃), mp 178°C; IR (KBr) 3600-3000, 1730, 1506; ¹H NMR (DMSO-d₆) 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, d, J = 10.75, 7.32), 2.32 (1H, dt, J = 10.75, 7.32), 0.88 (3H, t, J = 7.32); ¹³C NMR (DMSO-d₆) 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 (CHCl₃), mp 150°C; IR (KBr) 3600-3000, 1730, 1704; ¹H NMR (DMSO-d₆) 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 = 15.13), 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); ¹³C NMR (DMSO-d₆) 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 (CHCl₃), mp 156°C; IR (KBr) 3600-3200, 1730, 1704; ¹H NMR (DMSO-d₆) 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, s, J = 6.35); ¹³C NMR (DMSO-d₆) 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 (3b): colorless needles (ethanol), mp 160°C; IR (KBr) 3600-3200, 1720, 1710; ^1H 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); ^13C 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; ^1H 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); ^13C 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 (3d): colorless needles (ethanol), mp 149°C; IR (KBr) 3600-3000, 1732, 1706; ^1H 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); ^13C NMR (DMSO-d_{6}) 170.4, 165.8, 143.3, 140.8, 135.1, 132.4, 132.0, 128.5 (2C), 128.4 (2C), 127.3 (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_{29}H_{24}NO_{6}Cl_{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; ^1H 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); ^13C 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_{29}H_{24}NO_{6}F_{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; ^1H 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$_{25}$N$_{6}$O$_{6}$: 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$_{23}$N$_{6}$O$_{6}$: 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$_2$Cl$_2$-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$_{27}$N$_{6}$O$_{6}$: 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$_2$Cl$_2$-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$_{29}$N$_{6}$O$_{6}$: 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, t, 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$_{23}$N$_{6}$O$_{6}$: 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-Diarylethenes (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 60F254) with 1% MeOH-CH2Cl2 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 (CH2Cl2-hexane), mp 84°C; IR (CHCl3) 1770, 1740, 1710; 1H NMR (CDCl3) 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); 13C NMR (CDCl3) 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 C28H25NO4: 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 (CH2Cl2-hexane), mp 149°C; IR (CHCl3) 1773, 1740, 1710; 1H NMR (CDCl3) 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); 13C NMR (CDCl3) 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 C30H29NO4: 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 (CH2Cl2-hexane), mp 119°C; IR (CHCl3) 1771, 1740, 1710; 1H NMR (CDCl3) 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); 13C NMR (CDCl3) 194.2, 167.2, 157.2, 159.7, 159.5, 145.4, 133.9, 133.8, 131.0, 130.6 (2C), 128.1 (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 C30H29NO6: 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 (6ca): colorless microcrystals (CH2Cl2-hexane), mp 102-103°C; IR (CHCl3) 1776, 1740, 1710; 1H NMR (CDCl3) 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); 13C NMR (CDCl3) 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 C28H23NO4F2: 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 (CH₂Cl₂-hexane), mp 84 °C; IR (CHCl₃) 1773, 1760, 1745, 1714; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₃₀H₂₉N⁰₆: 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 (CH₂Cl₂-hexane), mp 102-103 °C; IR (CHCl₃) 1774, 1760, 1742, 1716; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₃₀H₂₇N⁰₆Cl₂: C, 63.39; H, 4.79; N, 2.46. Found: C, 63.12; H, 4.98; N, 2.66.

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-diphenylbutanoic acid (8a; 46.5 mg, 71% yield). A similar reaction of 3ai (112 mg) gave 8i (25 mg, 40% yield).

2-Ethoxycarbonyl-4,4-diphenylbutanoic acid (8a): colorless prisms (benzene-hexane), mp 67 °C (lit., 21 mp 67.4-68.5 °C); IR (CHCl₃) 1782, 1735; ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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-diphenylbutanoic acid (8i): colorless needles (CHCl₃-hexane), mp 123 °C (lit., 22 mp 123-124 °C); IR (CHCl₃) 2224, 1785; ¹H NMR (CDCl₃) 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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REFERENCES AND NOTES

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