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# SYNTHESIS OF PEROXYLACTONES USING Mn(III)-CATALYZED AEROBIC OXIDATION

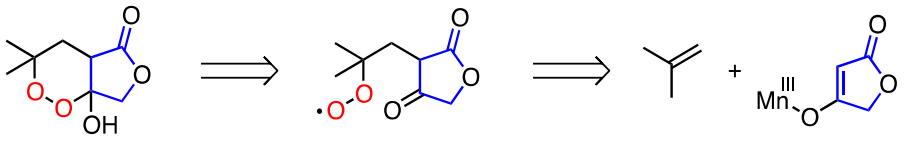
**Md. Aminul Haque and Hiroshi Nishino***

Department of Chemistry, Graduate School of Science and Technology,
Kumamoto University, Kurokami 2-39-1, Kumamoto 860-8555, Japan
Fax: +81-96-342-3374; E-mail: nishino@sci.kumamoto-u.ac.jp

**Abstract** – The aerobic oxidation of tetronic acid in the presence of 1,1-disubstituted alkenes afforded hydroperoxyethyl-peroxylactones, while a similar reaction using 3-alkyl-substituted tetronic acids gave stable crystalline peroxylactones in good to excellent yields. The oxidation using a stoichiometric amount of manganese(III) acetate did not give the bicyclic lactone but the ethenyl- and/or ethyl-tetronic acid derivatives.

## INTRODUCTION

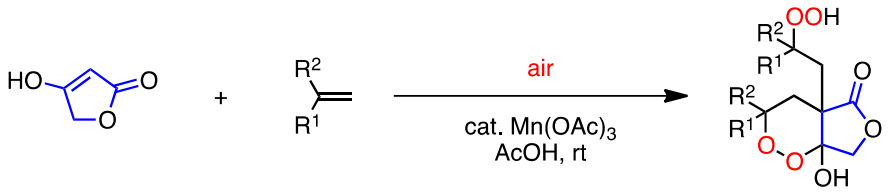
Many cyclic peroxides have been isolated from marine metabolites, terrestrial sources, steroids, and fatty acids.[1] These cyclic peroxides have various biological activities, for example, cytotoxic, antitumor, antimalarial, antifungal, antagonistic, antimicrobial, ichthyotoxic, antibacterial, etc. These activities seem to be attributable to the active decomposition products derived from the cleavage of the peroxy bond *in vivo*.[2] Although the peroxide linkage generally appears to be weak since the dissociation energy is estimated to be only 34 kcal/mol,[3] six-membered cyclic peroxides are unexpectedly stable in neutral and basic media, even in acidic solution, based on our experience.[4,5] Recently, Taylor et al. reported the synthesis of peroxylactones[6] and conversion into building blocks of Hagen's gland lactones[7] and natural products.[8] Plakortolides having a cytotoxic property were isolated from marine sponges[9] and used as the starting material of the building blocks.[6] The plakortolides consist of a 2,3,7-trioxabicyclo-[4.3.0]nonan-8-one skeleton, so we conceived the reaction of tetronic acids, a kind of cyclic $\beta$-keto esters, with alkenes under Mn(III)-catalyzed aerobic oxidation conditions to synthesize a similar trioxabicyclo[4.3.0]nonanone scaffold (Scheme 1).[4c,10] A commercially available tetronic acid (4-hydroxy-2(5*H*)-furanone) and its derivatives are also important as a core of the biologically active natural products such as the antibiotic, antiviral, antineoplastic, anticoagulant, insecticidal, acaricidal, antioxidant, and anti-inflammatory agents.[11] In this paper, we describe the synthesis of new 2,3,8-trioxabicyclo[4.3.0]nonan-7-ones, their characterization, and related reaction.



**Scheme 1.** Retrosynthetic Analysis of Peroxylactone

## RESULTS AND DISCUSSION

**Reaction of Tetronic Acid (1a) with 1,1-Disubstituted Alkenes 2a-j.** We initially examined the reaction of a commercially available tetronic acid (**1a**) with crystalline 1,1-bis(4-chlrorophenyl)ethene (**2a**) in the presence of manganese(III) acetate in acetic acid at room temperature in order to evaluate the aerobic oxidation. When the reaction was carried out at the molar ratio of **1a**:**2a**:$Mn(OAc)_3$ = 2:0.5:0.5, the desired peroxylactone **3a** was fortunately isolated in 8% yield (Scheme 2 and Table 1, Entry 1). Since the 1:1 stoichiometric product was not isolated, but the hydroperoxyethyl-peroxylactone **3a** was produced by the reaction of **1a** with double **2a**,[12] we focused on the synthesis of the hydroperoxyethyl-peroxylactone **3a**. After the optimization of the reaction conditions, the yield of **3a** was improved up to 58% (Entry 6).




**1a** **2a-j** **3a-d,f-i**

**a** : $R^1 = R^2 = 4\text{-}ClC_6H_4$
**b** : $R^1 = R^2 = 4\text{-}FC_6H_4$
**c** : $R^1 = R^2 = Ph$
**d** : $R^1 = R^2 = 4\text{-}MeC_6H_4$
**e** : $R^1 = R^2 = 4\text{-}MeOC_6H_4$
**f** : $R^1 = 4\text{-}ClC_6H_4$, $R^2 = 4\text{-}BrC_6H_4$
**g** : $R^1 = 4\text{-}ClC_6H_4$, $R^2 = Me$
**h** : $R^1 = Ph$, $R^2 = Me$
**i** : $R^1 = 4\text{-}MeC_6H_4$, $R^2 = Me$
**j** : $R^1 = R^2 = Et$

**Scheme 2.** Reaction of Tetronic Acid (**1a**) with 1,1-Disubstituted Alkenes **2a-j** under Mn(III)-Catalyzed Aerobic Oxidation Conditions

The structure of **3a** was deduced by spectroscopic methods. The characteristic hydroperoxy group in the $^1H$ NMR spectrum appeared at 11.44 ppm which shifted downfield in DMSO-$d_6$ because of the intramolecular hydrogen-bond with the ester carbonyl group,[12] and three pairs of the geminal AB quartet appeared at 4.48 and 3.84 ppm ($J$ = 10.1 Hz), 3.18 and 2.87 ppm ($J$ = 14.7 Hz), and 3.00 and 2.43 ppm ($J$ = 14.4 Hz), respectively, assigned to the three methylene protons. In the $^{13}C$ NMR spectrum, only one carbonyl carbon appeared at 172.8 ppm due to the ester carbonyl group, and three characteristic quaternary carbons attached to the peroxy bonds were revealed at 103.2, 85.3, and 82.9 ppm. Therefore,

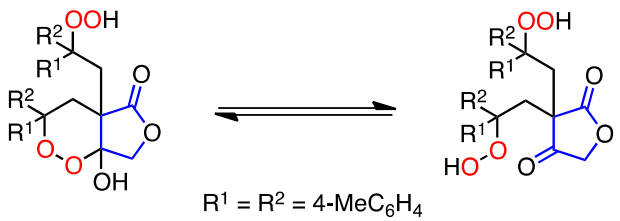
**Table 1.** Reaction of Tetronic Acid (**1a**) with 1,1-Disubstituted Alkenes **2a-j** in the Presence of $Mn(OAc)_3$[a]

| Entry | **2** | R | **1a**:**2**:$Mn(OAc)_3$ | Time/h | **3**/Yield/%[b] |
|---|---|---|---|---|---|
| 1 | **2a** | : $R^1 = R^2 = 4\text{-}ClC_6H_4$ | 2:0.5:0.5 | 14 | **3a** (8) |
| 2 | **2a** | : $R^1 = R^2 = 4\text{-}ClC_6H_4$ | 2:1:0.5 | 9 | **3a** (18) |
| 3 | **2a** | : $R^1 = R^2 = 4\text{-}ClC_6H_4$ | 1:1:0.5 | 4 | **3a** (31) |
| 4 | **2a** | : $R^1 = R^2 = 4\text{-}ClC_6H_4$ | 1:1:0.5 | 14 | **3a** (38) |
| 5 | **2a** | : $R^1 = R^2 = 4\text{-}ClC_6H_4$ | 0.5:1:0.1 | 11 | **3a** (35) |
| 6 | **2a** | : $R^1 = R^2 = 4\text{-}ClC_6H_4$ | 0.5:1:0.25 | 11 | **3a** (58) |
| 7 | **2b** | : $R^1 = R^2 = 4\text{-}FC_6H_4$ | 0.5:1:0.25 | 12 | **3b** (51) |
| 8 | **2c** | : $R^1 = R^2 = Ph$ | 0.5:1:0.25 | 11 | **3c** (58) |
| 9 | **2d** | : $R^1 = R^2 = 4\text{-}MeC_6H_4$ | 0.5:1:0.25 | 11 | **3d** (35)[c] |
| 10 | **2e** | : $R^1 = R^2 = 4\text{-}MeOC_6H_4$ | 0.5:1:0.25 | 12 | no reaction[d] |
| 11 | **2f** | : $R^1 = 4\text{-}ClC_6H_4$, $R^2 = 4\text{-}BrC_6H_5$ | 0.5:1:0.25 | 13 | **3f** (43)[e] |
| 12 | **2g** | : $R^1 = 4\text{-}ClC_6H_4$, $R^2 = Me$ | 0.5:1:0.25 | 13 | **3g** (40)[e] |
| 13 | **2h** | : $R^1 = Ph$, $R^2 = Me$ | 0.5:1:0.25 | 15 | **3h** (80)[e] |
| 14 | **2i** | : $R^1 = 4\text{-}MeC_6H_4$, $R^2 = Me$ | 0.5:1:0.25 | 11 | **3i** (58)[e] |
| 15 | **2j** | : $R^1 = R^2 = Et$ | 0.5:1:0.25 | 12 | complex mixture[f] |

[a] The reaction of **1a** (0.5 mmol) with **2** was carried out in acetic acid (20 mL) at room temperature in air.
[b] The yield based on the tetronic acid (**1a**) used.
[c] An equlibrium mixture of hydroperoxyethyl-peroxylactone **3d** and bishydroperoxide **3d'** was obtained as shown in Scheme 2.
[d] All the alkenes **2e** were recovered after the reaction.
[e] A stereoisomeric mixture was obtained, one of which was isolated in every case.
[f] An intractable mixture was obtained and no product could be isolated.

the structure of **3a** was determined to be 6-[2,2-bis(4-chlorophenyl)-2-hydroperoxyethyl]-4,4-bis(4-chlorophenyl)-1-hydroxy-2,3,8-trioxabicyclo[4.3.0]nonan-7-one based on the spectroscopic data including the HMQC spectrum and the elemental analysis.

With the optimized conditions in hand, we applied the reaction to various 1,1-disubstituted alkenes **2b-j**, and the desired hydroperoxyethyl-peroxylactones **3b-d**,**f-i** were obtained in moderate to good yields (Scheme 1 and Table 1, Entries 7-9,11-14). From the reaction with **2a-c**, only one isomer each **3a-c** probably due to energetically advantageous *cis*-fused peroxylactones was produced (Entries 6-8).[13,14] The product **3d** (Entry 9) existed as an equilibrium mixture of hydroperoxyethyl-peroxylactone **3d** and bishydroperoxide **3d'** in both $CDCl_3$ and DMSO-$d_6$ on the NMR time scale (Scheme 3). The reaction with **2f-i** also gave a stereoisomeric mixture of the corresponding hydroperoxyethyl-peroxylactones **3f-i** in good yields (Entries 11-14), one of which could be isolated. Surprisingly, the reaction with **2e** having

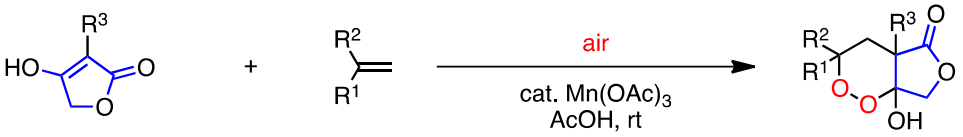



**3d** **3d'**

**Scheme 3.** Equilibrium of the Product **3d**

electron-donating substituents did not proceed and the alkene **2e** was recovered (Entry 10). The reaction with 2-ethyl-1-butene (**2j**) resulted in an intractable mixture (Entry 15).

**Reaction of 3-Substituted Tetronic Acids 1b-g with Various Alkenes 2a-l.** In order to prevent the double attack of the alkenes **2** on the tetronic acid (**1a**), we planned the reaction using 3-substituted tetronic acids. The 3-substituted tetronic acids **1b-g** were prepared by bromination of the corresponding 2-alkyl-3-oxobutanoates with bromine followed by cyclization.[15] With the 3-substituted tetronic acids **1b-g** in hand, we explored the aerobic oxidation of 3-methyltetronic acid (**1b**) using 1,1-diphenylethene (**2c**) (Scheme 4). When the reaction was carried out using one equivalent of manganese(III) acetate, the desired peroxylactone **4bc** was obtained in 85% yield (Table 2, Entry 3). After optimizing the reaction conditions, the highest yield of **4bc** (95%) was achieved using a catalytic amount of manganese(III) acetate (Entry 5). The structure of **4bc** was assigned by the spectroscopic method. The $^{1}$H NMR spectrum showed two specific pairs of geminal AB quartets at 4.22 and 3.95 ppm ($J$ = 10.5 Hz), 3.41 and 2.40 ppm ($J$ = 14.4 Hz), respectively, and the characteristic two quaternary carbons attached to an endoperoxy group appeared at 103.1 and 84.3 ppm in the $^{13}$C NMR spectrum. Therefore, the structure was determined to be 1-hydroxy-6-methyl-4,4-diphenyl-2,3,8-trioxabicyclo[4.3.0]nonan-7-one, and the elemental analysis also agreed with the structure. Since we were delighted to obtain the desired peroxylactone, we examined the reaction using other 3-alkyl-substituted tetronic acids **1c-g** and alkenes **2a-l**. All the reactions gave the




**1b-g** **2a-l** **4**

**1b** : $R^3$ = Me
**1c** : $R^3$ = Et
**1d** : $R^3$ = *i*-Pr
**1e** : $R^3$ = Bu
**1f** : $R^3$ = Bn
**1g** : $R^3$ = *n*-$C_5H_{11}$

**2a** : $R^1$ = $R^2$ = 4-$ClC_6H_4$
**2b** : $R^1$ = $R^2$ = 4-$FC_6H_4$
**2c** : $R^1$ = $R^2$ = Ph
**2d** : $R^1$ = $R^2$ = 4-$MeC_6H_4$
**2e** : $R^1$ = $R^2$ = 4-$MeOC_6H_4$
**2f** : $R^1$ = 4-$ClC_6H_4$, $R^2$ = 4-$BrC_6H_4$
**2g** : $R^1$ = 4-$ClC_6H_4$, $R^2$ = Me
**2h** : $R^1$ = Ph, $R^2$ = Me
**2i** : $R^1$ = 4-$MeC_6H_4$, $R^2$ = Me
**2j** : $R^1$ = $R^2$ = Et
**2k** : $R^1$ = Ph, $R^2$ = 2-thienyl
**2l** : $R^1$ = Ph, $R^2$ = H

**4ba** : $R^1$ = $R^2$ = 4-$ClC_6H_4$, $R^3$ = Me
**4bb** : $R^1$ = $R^2$ = 4-$FC_6H_4$, $R^3$ = Me
**4bc** : $R^1$ = $R^2$ = Ph, $R^3$ = Me
**4bd** : $R^1$ = $R^2$ = 4-$MeC_6H_4$, $R^3$ = Me
**4be** : $R^1$ = $R^2$ = 4-$MeOC_6H_4$, $R^3$ = Me
**4bf** : $R^1$ = 4-$ClC_6H_4$, $R^2$ = 4-$BrC_6H_4$, $R^3$ = Me
**4bg** : $R^1$ = 4-$ClC_6H_4$, $R^2$ = $R^3$ = Me
**4bh** : $R^1$ = Ph, $R^2$ = $R^3$ = Me
**4bi** : $R^1$ = 4-$MeC_6H_4$, $R^2$ = $R^3$ = Me
**4bk** : $R^1$ = Ph, $R^2$ = 2-Thienyl, $R^3$ = Me
**4bl** : $R^1$ = Ph, $R^2$ = H, $R^3$ = Me
**4cc** : $R^1$ = $R^2$ = Ph, $R^3$ = Et
**4dc** : $R^1$ = $R^2$ = Ph, $R^3$ = *i*-Pr
**4ec** : $R^1$ = $R^2$ = Ph, $R^3$ = Bu
**4fc** : $R^1$ = $R^2$ = Ph, $R^3$ = Bn
**4ga** : $R^1$ = $R^2$ = 4-$ClC_6H_4$, $R^3$ = *n*-$C_5H_{11}$

**Scheme 4.** Reaction of Various 3-Substituted Tetronic Acids **1b-g** with Alkenes **2a-l** under the Mn(III)-Catalyzed Aerobic Oxidation Conditions

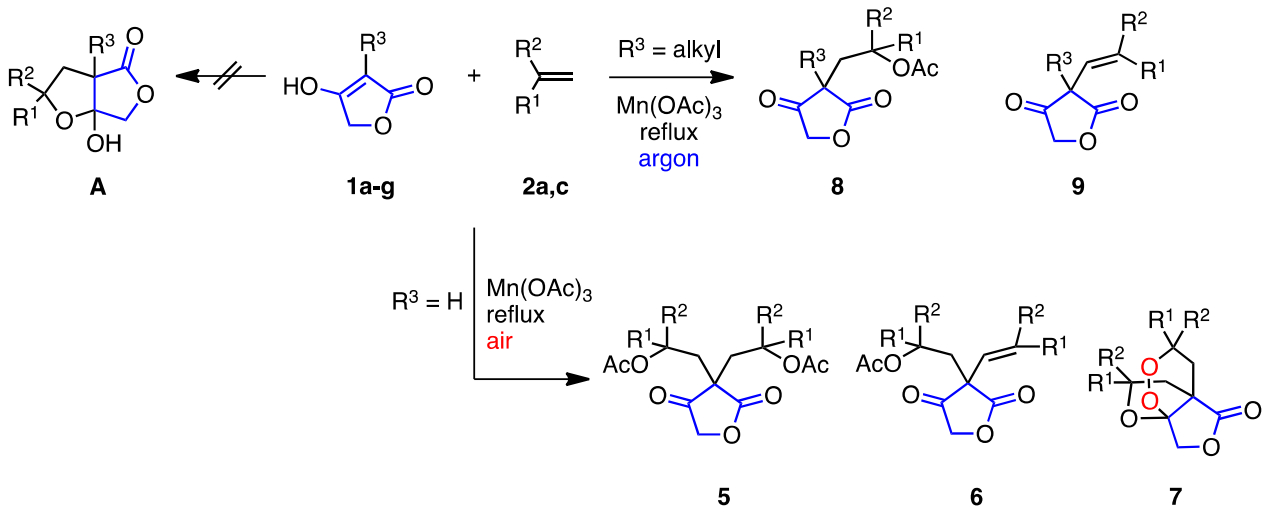
**Table 2.** Reaction of Substituted Tetronic Acids **1b-g** with Various 1,1-Disubstituted Alkenes **2a-j** in the Presence of $Mn(OAc)_3$[a]

| Entry | Tetronic acid | Alkene | **1**:**2**:$Mn(OAc)_3$ | Time/h | Product (yield/%)[b] |
|---|---|---|---|---|---|
| 1 | **1b** | **2a** | 1:1:0.2 | 11 | **4ba** (83) |
| 2 | **1b** | **2b** | 1:1:0.2 | 10 | **4bb** (84) |
| 3 | **1b** | **2c** | 1:1:1 | 12 | **4bc** (85) |
| 4 | **1b** | **2c** | 1:1:0.1 | 12 | **4bc** (90) |
| 5 | **1b** | **2c** | 1:1:0.2 | 11 | **4bc** (95) |
| 6 | **1b** | **2d** | 1:1:0.2 | 12 | **4bd** (83) |
| 11 | **1b** | **2e** | 1:1:0.2 | 11 | **4be** (80) |
| 7 | **1b** | **2f** | 1:1:0.2 | 13 | **4bf** (87) |
| 8 | **1b** | **2g** | 1:1:0.2 | 12 | **4bg** (85)[c] |
| 9 | **1b** | **2h** | 1:1:0.2 | 11 | **4bh** (97)[c] |
| 10 | **1b** | **2i** | 1:1:0.2 | 13 | **4bi** (84)[c] |
| 12 | **1b** | **2j** | 1:1:0.2 | 12 | complex mixture[d] |
| 13 | **1b** | **2k** | 1:1:0.2 | 12 | **4bk** (77)[c] |
| 14 | **1b** | **2l** | 1:1:0.2 | 11 | **4bl** (94)[c] |
| 15 | **1c** | **2c** | 1:1:0.2 | 11 | **4cc** (82) |
| 16 | **1d** | **2c** | 1:1:0.2 | 11 | **4dc** (78) |
| 17 | **1e** | **2c** | 1:1:0.2 | 11 | **4ec** (71) |
| 18 | **1f** | **2c** | 1:1:0.2 | 3 | **4fc** (80) |
| 19 | **1g** | **2a** | 1:1:0.2 | 11 | **4ga** (89) |

[a] The reaction of **1** (1 mmol) with **2** (1 mmol) was carried out in acetic acid (20 mL) in air.
[b] The yield based on the alkene **2** used.
[c] Two isomers were separated and characterized.
[d] An intractable mixture was obtained and no product could be isolated.

desired peroxylactones **4** in good to excellent yields except for 2-ethyl-1-butene (**2j**) which afforded an inseparable mixture (Table 2, Entries 1, 2, 6-19). When the 1,1-disubstututed alkenes **2g**, **2h**, **2i**, **2k**, and **2l** having a different substituent were used in the reaction, two diastereomers were isolated and characterized (Entries 8-10, 13, and 14). Surprisingly, 3-benzyltetronic acid was consumed within 3 h, giving the peroxylactone **4fc** in 80% yield (Entry 18).

**Reaction at Elevated Temperature.** Concave bicyclic lactones, such as Hagen's gland lactones, are structurally and biologically interesting,[7,16] therefore, it was speculated that the bicyclic lactones such as **A** in Scheme 5 would be formed by the Mn(III)-based oxidative addition of tetronic acids to alkenes in the absence of molecular oxygen. We then explored the teronic acids with alkenes using a stoichiometric amount of manganese(III) acetate at elevated temperature. As a result, the reaction of tetronic acid (**1a**) with the 1,1-disubstituted alkenes **2a** and **2c** did not give the bicyclic lactone **A**, but the teronic acid (**1a**) underwent double alkylation to afford the diethyl- and/or ethenyl-ethyl-substituted tetronic acids **5** and/or **6** along with peroxypropellane **7** when **2c** was used (Scheme 5 and Table 3, Entries 1 and 2).[4c,12,14,17] The formation of the peroxypropellane **7** could be avoided by the reaction under an argon atmosphere.[17] The 3-alkyl-substituted tetronic acids **1b-g** also underwent substitution to produce the corresponding ethyl- **8** and/or ethenyl-tetronic acids **9** (Table 3, Entries 3-9).



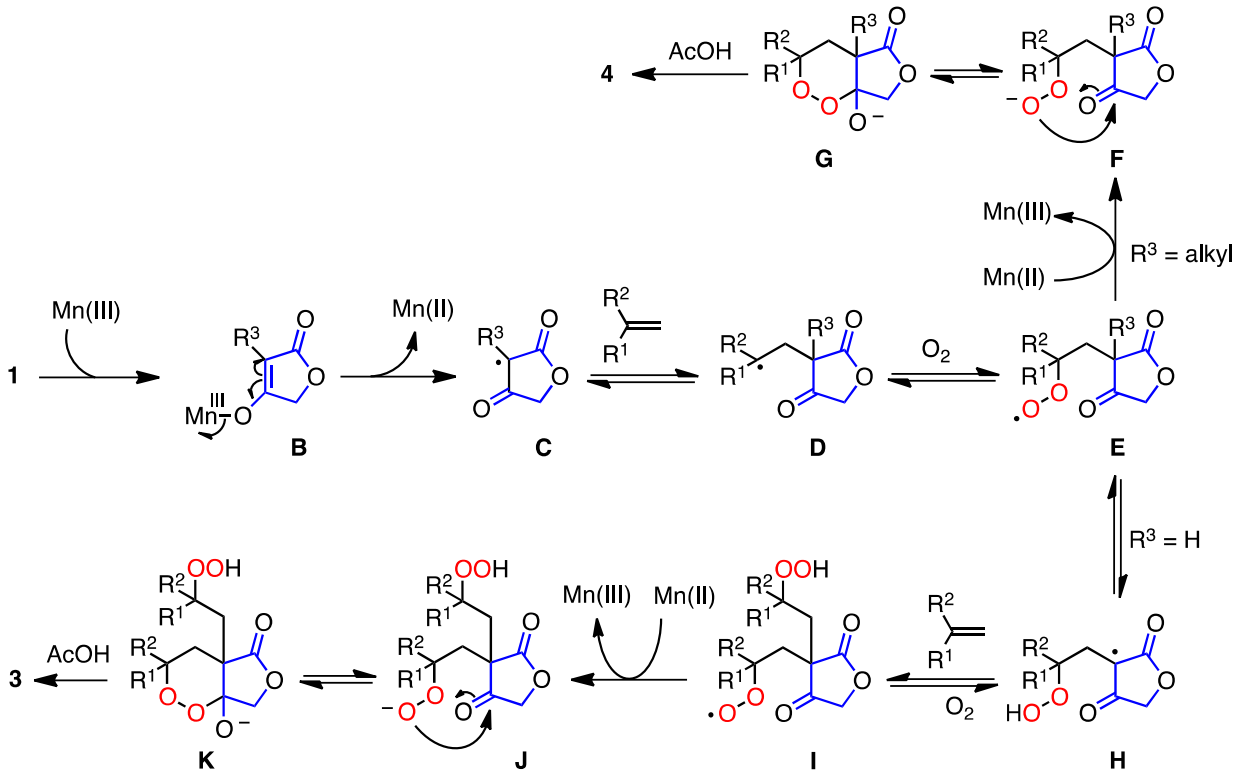

**Scheme 5.** Reaction of Tetronic Acids **1a-g** with Alkenes **2a**,**c** at Elevated Temperature

**Table 3.** Oxidation of Tetronic acids **1a-g** with $Mn(OAc)_3$ in the Presence of 1,1-Disubstituted Alkenes **2a**,**c**[a]

| Entry | Tetronic acid | Alkene | **1**:**2**:$Mn(OAc)_3$ | Time/min | Product (yield/%) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | **5**[b] | **6**[b] | **7**[b] | **8**[c] | **9**[c] |
| 1 | **1a** : $R^3$ = H | **2a** : $R^1$ = $R^2$ = 4-$ClC_6H_4$ | 1:2:4 | 9 | 32 | 13 | | | |
| 2 | **1a** : $R^3$ = H | **2c** : $R^1$ = $R^2$ = Ph | 1:2:4 | 5 | 20 | | 12 | | |
| 3 | **1b** : $R^3$ = Me | **2a** : $R^1$ = $R^2$ = 4-$ClC_6H_4$ | 2:0.5:2 | 4 | | | | 60 | 8 |
| 4 | **1b** : $R^3$ = Me | **2c** : $R^1$ = $R^2$ = Ph | 2:0.5:2 | 5 | | | | 32 | 25 |
| 5 | **1c** : $R^3$ = Et | **2c** : $R^1$ = $R^2$ = Ph | 2:0.5:2 | 3 | | | | 51 | 11 |
| 6 | **1d** : $R^3$ = *i*-Pr | **2c** : $R^1$ = $R^2$ = Ph | 2:0.5:2 | 3 | | | | 72 | 18 |
| 7 | **1e** : $R^3$ = Bu | **2c** : $R^1$ = $R^2$ = Ph | 1:0.5:2 | 13 | | | | | 70 |
| 8 | **1f** : $R^3$ = Bn | **2a** : $R^1$ = $R^2$ = 4-$ClC_6H_4$ | 2:0.5:2 | 5 | | | | 53 | 13 |
| 9 | **1g** : $R^3$ = *n*-$C_5H_{11}$ | **2c** : $R^1$ = $R^2$ = Ph | 2:0.5:2 | 13 | | | | 3 | 35 |

[a] The oxidation of a mixture of **1** (2 mmol) and **2** with $Mn(OAc)_3$ was carried out in acetic acid (20 mL) at reflux temperature.
[b] The yield based on the tetronic acid (**1a**) used.
[c] The yield based on the alkene **2** used.

**Reaction Pathway.** Although the mechanism for the formation of the endoperoxides **3** and **4** in the Mn(III)-catalyzed aerobic oxidation and the ethenyl- **6**, **9** and/or ethyl-tetronic acid derivatives **5**, **8** in the Mn(III)-mediated oxidation is well-documented in the literature,[18] in order to comprehend the present reactions, the reaction pathway is outlined in Schemes 6 and 7. The tetronic acid **1** underwent complexation with Mn(III) catalyst to produce enolate complex **B** followed by single electron-transfer oxidation and addition with the alkene **2**, giving radical **D** (Scheme 6). The radical **D** would be trapped by the dissolved molecular oxygen to form peroxy radical **E**, which would be reduced by Mn(II) species followed by cyclization and protonation to produce the peroxylactone **4**, when the substituent $R^3$ is an alkyl group. On the other hand, when the $R^3$ group is hydrogen, the peroxy radical **E** would prefer to undergo hydrogen abstraction to produce hydroperoxyethyl radical **H**, and finally, the hydroperoxyethyl-peroxylactone **3** would be obtained *via* similar steps from **E** to **4** (Scheme 6). Although it is not clear the reaction of **1a** with **2e** did not occur at this moment (Table 1, Entry 10), the equilibrium



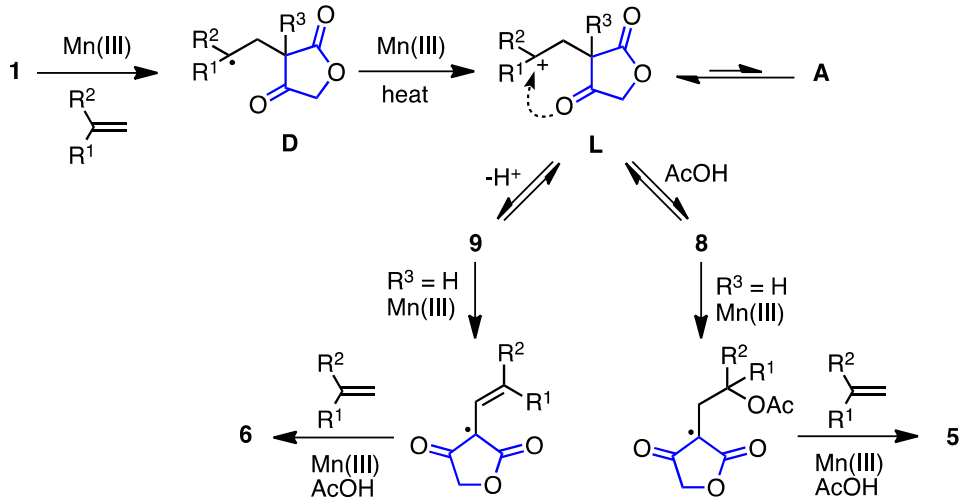

**Scheme 6.** Reaction Pathway of the Mn(III)-Catalyzed Aerobic Oxidation

from **C** to **I** in Scheme 6 might lie so far to the left since the electron-rich alkene **2e** might be considerably stable under the conditions. In addition, the radical reaction would not be controlled in the reaction with **2j** since the radical intermediate **D** would not be sufficiently stabilized by the inductive effect of the alkyl substituent ($R^1$ = $R^2$ = Et). Therefore, the reaction gave an intractable mixture (Table 1, Entry 15 and Table 2, Entry 12).

When the reaction was carried out at elevated temperature using a stoichiometric amount of the oxidant, the radical **D** would be preferentially oxidized to produce the corresponding cation **L** (Scheme 7). The cation **L** did not cyclize with the *keto*-carbonyl oxygen probably because of the steric strain and the instability of the hemiacetal **A** in boiling acetic acid, but predominantly would be attacked by the solvent or deprotonate to produce **8** or **9**. When the $R^3$ group is hydrogen, a similar oxidation would be repeated to afford **5** and **6**.

## CONCLUSION

We achieved the synthesis of the peroxylactones **3** and **4** which might be important building blocks of some synthetic targets. The peroxylactones could be used for the construction of Hagen's gland lactone analogues,[19] or converted into the corresponding diols as a building block.[6] The direct synthesis of the concave bicyclic lactones **A** failed. Since the peroxylactones are stable and handy, the biological screening of the peroxylactones **3** and **4** are underway.




**Scheme 7.** Reaction Pathway of the Mn(III)-Mediated Oxidation at Elevated Temperature

## EXPERIMENTAL

**General Information.** Melting points were taken using a Yanagimoto micromelting point apparatus and were not corrected. The NMR spectra were recorded using a JNM AL300 or ECX 500 FT-NMR spectrometer at 300 or 500 MHz for $^{1}$H and 75 or 125 MHz for $^{13}$C, with tetramethylsilane as the internal standard. The chemical shifts are reported in $\delta$ values (ppm) and the coupling constants in Hz. The IR spectra were measured in chloroform or KBr using a Shimadzu 8400 FT IR spectrometer and expressed in cm$^{-1}$. The EI MS spectra were measured by a Shimadzu QP-5050A gas chromatograph-mass spectrometer with the ionizing voltage of 70 eV. The high-resolution mass spectra and the elemental analysis were performed at the Instrumental Analysis Center, Kumamoto University, Kumamoto, Japan. Manganese(II) acetate tetrahydrate, $Mn(OAc)_2$•$4H_2O$, was purchased from Wako Pure Chemical Ind., Ltd. Manganese(III) acetate dehydrate, $Mn(OAc)_3$•$2H_2O$, was prepared according to the modified method described in the literature.[20] The 1,1-disubstituted ethenes **2a-2i** and **2k** were prepared by the reaction of the corresponding acetophenones with arylmagnesium bromides followed by dehydration. Tetronic acid (**1a**), 2-ethyl-1-butene (**2j**) and styrene (**2l**) were purchased from Tokyo Chemical Industry Co., Ltd., and used as received.

**Preparation of 3-Substituted Tetronic Acids (1b-g).**

4-Hydroxy-3-methyl-2(5*H*)-furanone (**1b**) was prepared as follows.[15a] Bromine (5.85g, 36.5 mmol) in $CHCl_3$ (5 mL) was dropwise added to a stirred solution of ethyl $\alpha$-methylacetoacetate (5g, 34.5 mmol) in $CHCl_3$ (17 mL) at 0 °C, and the reaction mixture was further stirred for 1 h at rt. Evaporation of the solvent gave the residue, which was heated for 2 h at 130 °C. After cooling, the solid residue was washed with hexane and then recrystallized from methanol to give **1b** (2.7 g; 68%) as colorless needles. The other 3-substituted tetronic acids **1c-g** were prepared by a method similar to that already described.

**4-Hydroxy-3-methyl-2(5*H*)-furanone (1b):** Colorless needles (from MeOH); mp 190-191 °C (lit.[15a] mp 190-191 °C); IR (KBr) $\nu$ 1749, 1681 (C=O); $^1$H NMR (DMSO-$d_6$) $\delta$ = 11.81 (1H, br s, OH), 4.57 (2H, s, $CH_2$-C=O), 1.59 (3H, s, Me); $^{13}$C NMR (DMSO-$d_6$); $\delta$ = 175.2 (C-4), 172.9 (C-2, C=O), 94.4 (C-3), 66.5 (C-5, $CH_2$), 5.9 (Me).

**3-Ethyl-4-hydroxy-2(5*H*)-furanone (1c):** Colorless needles (from $CHCl_3$/hexane); mp 126-127 °C (lit.[15e,f] mp 127-129 °C); IR (KBr) $\nu$ 1730, 1654 (C=O); $^1$H NMR (DMSO-$d_6$) $\delta$ = 10.62 (1H, br s, OH), 4.62 (2H, s, $CH_2$-C=O), 2.17 (2H, q, $J$ = 7.8 Hz, $CH_2$), 1.01(3H, t, $J$ = 7.8 Hz, Me); $^{13}$C NMR (DMSO-$d_6$) $\delta$ = 179.2 (C-4), 174.4 (C-2, C=O), 102.7 (C-3), 67.9 (C-5, $CH_2$), 14.4 ($CH_2$), 12.4 (Me).

**3-Isopropyl-4-hydroxy-2(5*H*)-furanone (1d):** Colorless needles (from EtOAc/hexane); mp 121-123 °C (lit.[15c] mp 120-123 °C); IR (KBr) $\nu$ 1724, 1662 (C=O); $^1$H NMR (DMSO-$d_6$) $\delta$ = 10.48 (1H, br s, OH), 4.64 (2H, s, $CH_2$-C=O), 2.74 (1H, m, CH), 1.19 (6H, d, $J$ = 6.9 Hz, 2Me); $^{13}$C NMR (DMSO-$d_6$) $\delta$ = 178.4 (C-4), 173.8 (C-2, C=O), 106.1 (C-3), 67.5 (C-5, $CH_2$), 22.8 (CH), 20.2 (2Me).

**3-Butyl-4-hydroxy-2(5*H*)-furanone (1e):** Colorless needles (from $CHCl_3$/hexane); mp 121-122 °C (lit.[15d] 121-123 °C); IR (KBr) $\nu$ 1732, 1658 (C=O); $^1$H NMR (DMSO-$d_6$) $\delta$ = 10.66 (1H, br s, OH), 4.62 (2H, s, $CH_2$-C=O), 2.14 (2H, t, $J$ = 7.2 Hz, $CH_2$), 1.30 (4H, m, $2CH_2$), 0.83(3H, t, $J$ = 7.2 Hz, Me); $^{13}$C NMR (DMSO-$d_6$) $\delta$ = 179.5 (C-4), 174.8 (C-2, C=O), 101.4 (C-3), 67.9 (C-5, $CH_2$), 29.9, 22.4, 20.6 ($CH_2$), 13.7 (Me).

**3-Benzyl-4-hydroxy-2(5*H*)-furanone (1f):** Colorless amorphous solid[15g]; IR (KBr) $\nu$ 1747, 1672 (C=O); $^1$H NMR (DMSO-$d_6$) $\delta$ = 12.14 (1H, br s, OH), 7.29-7.14 (5H, m, arom H), 4.66 (2H, s, $CH_2$-C=O), 3.42 (2H, s, $PhCH_2$); $^{13}$C NMR (DMSO-$d_6$) $\delta$ = 174.8 (C-4), 174.1 (C-2, C=O), 139.6, 128.3, 128.1, 125.9 (arom C), 98.4 (C-3), 66.6 (C-5, $CH_2$), 26.6 ($CH_2$).

**4-Hydroxy-3-pentyl-2(5*H*)-furanone (1g):** Colorless needles (from $CHCl_3$/hexane); mp 112-113 °C (lit.[15d] mp 112-113 °C); IR (KBr) $\nu$ 1737, 1662 (C=O); $^1$H NMR (DMSO-$d_6$) $\delta$ = 11.74 (1H, br s, OH), 4.56 (2H, s, $CH_2$-C=O), 2.10-1.99 (2H, br, $CH_2$), 1.38-1.23 (6H, br, $3CH_2$), 0.86-0.84 (3H, br, Me); $^{13}$C NMR (DMSO-$d_6$) $\delta$ = 174.9 (C-4), 173.13 (C-2, C=O), 99.0 (C-3), 66.3 (C-5, $CH_2$), 30.9, 27.1, 21.8, 20.7 ($CH_2$), 13.9 (Me).

**Reaction of Tetronic Acid (1a) with 1,1-Disubstituted Alkenes 2a-j.** To a solution of the tetronic acid (**1a**) (0.5 mmol) and 1,1-disubstituted alkene **2** (1 mmol) in glacial acetic acid (20 mL), manganese(III) acetate dehydrate (0.25 mmol) was added. The mixture was stirred at rt in air for 11-15 h, and then the reaction was quenched by adding water (20 mL) to the mixture. The aqueous reaction mixture was extracted three times with $CH_2Cl_2$ (30 mL) and the combined extracts were washed with water, then a saturated aqueous solution of $NaHCO_3$, dried over anhydrous $MgSO_4$, and concentrated to dryness. The residue was purified by silica gel column chromatography while eluting with the appropriate solvent. The

results are shown in Table 1. The products **3f-i** were obtained as a stereoisomeric mixture. Although we could not determine the diastereomeric ratio, one of the diastereomers was isolated and characterized after chromatographic separation. The data of the isolated diastereomers **3f-i** were described (vide infra).

**6-[2,2-Bis(4-chlorophenyl)-2-hydroperoxyethyl]-4,4-bis(4-chlorophenyl)-1-hydroxy-2,3,8-trioxabicyclo[4.3.0]nonan-7-one (3a):** Yield (190.5 mg, 58%); $R_f$ = 0.65 ($Et_2O$/hexane 7:3 v/v); colorless needles (from $CHCl_3$/hexane); mp 177-178 °C; IR (KBr) $\nu$ 3600-3100 (OOH, OH), 1757 (C=O); $^1$H NMR (DMSO-$d_6$) $\delta$ = 11.44 (1H, s, OOH), 8.16 (1H, s, OH), 7.44-7.11 (16H, m, arom H), 4.48 (1H, d, $J$ = 10.1 Hz, $H_a$-9), 3.84 (1H, d, $J$ = 10.1 Hz, $H_b$-9), 3.18 (1H, d, $J$ = 14.7 Hz, $H_a$-5), 3.00 (1H, d, $J$ = 14.4, $^a$$CH_2$), 2.87 (1H, d, $J$ = 14.7 Hz, $H_b$-5), 2.43 (1H, d, $J$ = 14.4 Hz, $^b$$CH_2$); $^{13}$C NMR (DMSO-$d_6$) $\delta$ = 172.8 (C=O), 143.4, 143.3, 142.7, 139.9, 132.5, 131.8, 131.6, 131.5 (arom C), 128.6, 128.4, 128.1, 127.8, 127.6, 126.8 (arom CH), 103.2 (C-1), 85.3 (quart C), 82.9 (C-4), 69.3 ($CH_2$), 44.3 (C-6), 38.4, 35.1 ($CH_2$). *Anal.* Calcd for $C_{32}H_{24}Cl_4O_7$•1/3$H_2O$: C, 57.51; H, 3.72. Found: C, 57.57; H, 3.81.

**6-[2,2-Bis(4-fluorophenyl)-2-hydroperoxyethyl]-4,4-bis(4-fluorophenyl)-1-hydroxy-2,3,8-trioxabicyclo[4.3.0]nonan-7-one (3b):** Yield (152 mg, 51%); $R_f$ = 0.49 ($Et_2O$/hexane 7:3 v/v); colorless microcrystals (from $CHCl_3$/hexane); mp 121-122 °C; IR (KBr) $\nu$ 3600-3100 (OOH, OH), 1774 (C=O); $^1$H NMR ($CDCl_3$) $\delta$ = 8.95 (1H, s, OOH), 7.38-6.88 (16H, m, arom H), 4.46 (1H, s, OH), 4.32 (1H, d, $J$ = 10.5 Hz, $H_a$-9), 3.87 (1H, d, $J$ = 10.5 Hz, $H_b$-9), 3.21 (1H, d, $J$ = 15.6 Hz, $H_a$-5), 3.03 (1H, d, $J$ = 14.7 Hz, $^a$$CH_2$), 2.96 (1H, d, $J$ = 15.6 Hz, $H_b$-5), 2.27 (1H, d, $J$ = 14.7 Hz, $^b$$CH_2$); $^{13}$C NMR ($CDCl_3$) $\delta$ = 175.0 (C=O), 163.6, 163.5, 160.5, 139.9, 139.5, 137.7, 134.9 (arom C), 128.7, 128.6, 127.9, 127.9, 127.8, 127.7, 127.0, 126.9, 115.6, 115.5, 115.4, 115.3, 115.2, 115.1, 114.8 (arom CH), 103.3 (C-1), 86.1 (quart C), 84.5 (C-4), 70.6 ($CH_2$), 44.9 (C-6), 40.7, 37.0 ($CH_2$). *Anal.* Calcd for $C_{32}H_{24}F_4O_7$: C, 64.43; H, 4.06. Found: C, 64.72; H, 4.27.

**6-(2-Hydroperoxy-2,2-diphenylethyl)-1-hydroxy-4,4-diphenyl-2,3,8-trioxabicyclo[4.3.0]nonan-7-one (3c):** Yield (150.9 mg, 58%); $R_f$ = 0.29 ($Et_2O$/hexane 7:3 v/v); colorless microcrystals (from $CHCl_3$/hexane); mp 112-114 °C; IR (KBr) $\nu$ 3600-3100 (OOH, OH), 1786 (C=O); $^1$H NMR ($CDCl_3$) $\delta$ = 8.99 (1H, s, OOH), 7.59-6.92 (20H, m, arom H), 4.67 (1H, s, OH), 4.30 (1H, d, $J$ = 10.5 Hz, $H_a$-9), 3.84 (1H, d, $J$ = 10.5 Hz, $H_b$-9), 3.21 (1H, d, $J$ = 15.6 Hz, $H_a$-5), 3.11 (1H, d, $J$ = 14.7 Hz, $^a$$CH_2$), 3.05 (1H, d, $J$ = 15.6 Hz, $H_b$-5), 2.32 (1H, d, $J$ = 14.7 Hz, $^b$$CH_2$); $^{13}$C NMR ($CDCl_3$) 175.4 (C=O), 144.6, 144.0, 142.2, 139.8 (arom C), 130.2, 128.6, 128.2, 127.8, 127.4, 127.3, 127.2, 126.7, 126.4, 126.0, 125.2, 124.9 (arom CH), 103.4 (C-1), 86.7 (quart C), 84.9 (C-4), 70.6 ($CH_2$), 45.0 (C-6), 40.6, 36.7 ($CH_2$). *Anal.* Calcd for $C_{32}H_{28}O_7$•1/2 $H_2O$: C, 72.03; H, 5.48. Found: C, 72.19; H, 5.73.

**6-[2-Hydroperoxy-2,2-bis(4-methylphenyl)ethyl]-1-hydroxy-4,4-bis(4-methylphenyl)-2,3,8-trioxabicyclo[4.3.0]nonan-7-one (3d):** Yield (101.6 mg, 35%); IR (KBr) $\nu$ 3600-3100 (OOH, OH), 1786 (C=O); $^1$H NMR ($CDCl_3$) the OOH group did not appeared; $\delta$ = 7.67-7.65 (4H, m, arom H), 7.28-6.99

(12H, m, arom H), 5.83 (1H, s, OH), 4.22 (1H, d, $J$ = 10.2 Hz, $H_a$-9), 4.09 (1H, d, $J$ = 10.2 Hz, $H_b$-9), 3.52 (1H, d, $J$ = 18.0 Hz, $H_a$-5), 3.09 (1H, d, $J$ = 18.0 Hz, $H_b$-5), 2.97 (1H, d, $J$ = 14.4 Hz, $^aCH_2$), 2.87 (1H, d, $J$ = 14.4 Hz, $^bCH_2$), 2.30 (3H, s, Me), 2.22 (9H, s, 3Me); $^{13}$C NMR ($CDCl_3$) 198.1 (C-4 keto carbonyl), 177.3 (C=O), 145.4, 141.6, 138.6, 137.5, 137.0, 133.3, 124.6 (arom C), 129.4, 129.2, 129.1, 128.8, 128.5, 126.2, 125.3, 124.5 (arom CH), 104.0 (C-1), 85.0 (quart C), 76.6 (C-4), 73.2 (C-9), 46.0 (C-6), 42.0 ($CH_2$), 36.7 (C-5), 31.7, 27.5 (Me); $^{13}$C NMR (DMSO-$d_6$) 196.7 (C-4 keto carbonyl), 177.1 (C=O), 144.1, 139.1, 136.4, 136.1, 133.4 (arom C), 129.8, 129.3, 129.1, 128.8, 128.5, 128.2, 125.7, 124.9 (arom CH), (C-1 missing), 84.1 (quart C), (C-4 missing), (C-9 missing), 44.7 (C-6), 43.8 ($CH_2$), (C-5 missing), 21.7, 21.0 (Me). *Anal.* Calcd for $C_{36}H_{36}O_7$•1/2$H_2O$: C, 73.33; H, 6.33. Found: C, 73.10; H, 6.03.

**6-[2-(4-Bromophenyl)-2-(4-chlorophenyl)-2-hydroperoxyethyl]-4-(4-bromophenyl)-4-(4-chlorophenyl)-1-hydroxy-2,3,8-trioxabicyclo[4.3.0]nonan-7-one (3f):** Yield (161.5 mg, 43%); $R_f$ = 0.48 (EtOAc/hexane 4:6 v/v); colorless needles (from $CHCl_3$/hexane); mp 160-162 °C; IR (KBr) $\nu$ 3550-3100 (OOH, OH), 1757 (C=O); $^1$H NMR (DMSO-$d_6$) $\delta$ = 11.46 (1H, s, OOH), 8.18 (1H, s, OH), 7.62-7.03 (16H, m, arom H), 4.48 (1H, d, $J$ = 10.5 Hz, $H_a$-9), 3.83 (1H, d, $J$ = 10.5 Hz, $H_b$-9), 3.18 (1H, d, $J$ = 15.0 Hz, $H_a$-5), 3.00 (1H, d, $J$ = 14.1 Hz, $^aCH_2$), 2.87 (1H, d, $J$ = 15.0 Hz, $H_b$-5), 2.42 (1H, d, $J$ = 14.1 Hz, $^bCH_2$); $^{13}$C NMR (DMSO-$d_6$) $\delta$ = 172.8 (C=O), 143.8, 143.2, 143.1, 142.6, 140.4, 139.9, 120.4, 120.2 (arom C), 131.3, 130.8, 130.5, 128.9, 128.7, 128.5, 128.4, 128.0, 127.8, 127.6, 127.0, 126.9, 126.7, 126.7 (arom CH), 103.2 (C-1), 85.3 (quart C), 82.8 (C-4), 69.3 ($CH_2$), 44.3 (C-6), 38.3, 35.0 ($CH_2$). *Anal.* Calcd for $C_{32}H_{24}Br_2Cl_2O_7$•1/2$H_2O$: C, 50.56; H, 3.31. Found: C, 50.67; H, 3.53.

**6-[2-(4-Chlorophenyl)-2-hydroperoxypropyl]-4-(4-chlorophenyl)-1-hydroxy-4-methyl-2,3,8-trioxabicyclo[4.3.0]nonan-7-one (3g):** Yield (94 mg, 40%); $R_f$ = 0.21 (EtOAc/hexane 3:7 v/v); colorless microcrystals (from $CHCl_3$/hexane); mp 81-83 °C; IR (KBr) $\nu$ 3600-3100 (OOH), 1770 (C=O); $^1$H NMR ($CDCl_3$) $\delta$ = 8.92 (1H, s, OOH), 7.38-7.21 (8H, m, arom H), 4.37 (1H, d, $J$ = 10.5 Hz, $H_a$-9), 4.16 (1H, s, OH), 3.79 (1H, d, $J$ = 10.5 Hz, $H_b$-9), 2.92 (1H, d, $J$ = 14.7 Hz, $H_a$-5), 2.49 (1H, d, $J$ = 15.6 Hz, $^aCH_2$), 2.31 (1H, d, $J$ = 15.6 Hz, $^bCH_2$), 1.92 (1H, d, $J$ = 14.7 Hz, $H_b$-5), 1.67 (3H, s, Me), 1.29 (3H, s, Me); $^{13}$C NMR ($CDCl_3$) $\delta$ = 174.7 (C=O), 140.4, 139.3, 133.6, 133.1, (arom C), 128.4, 128.1, 127.2, 126.7, (arom CH), 103.2 (C-1), 84.5 (quart C), 82.1 (C-4), 70.3 ($CH_2$), 44.7 (C-6), 43.4, 36.9 ($CH_2$), 31.6, 27.6 (Me). *Anal.* Calcd for $C_{22}H_{22}Cl_2O_7$•1/3$H_2O$: C, 55.59; H, 4.81. Found: C, 55.83; H, 5.06.

**6-[2-Hydroperoxy-2-phenylpropyl]-1-hydroxy-4-methyl-4-phenyl-2,3,8-trioxabicyclo[4.3.0]nonan-7-one (3h):** Yield (161 mg, 80%); $R_f$ = 0.26 (EtOAc/Hexane 3:7 v/v); colorless microcrystals (from $CHCl_3$/hexane); mp 89-91 °C; IR (KBr) $\nu$ 3650-3100 (OOH, OH), 1766 (C=O); $^1$H NMR ($CDCl_3$) $\delta$ = 8.88 (1H, s, OOH), 7.40-7.08 (10H, m, arom H), 4.43 (1H, s, OH), 4.27 (1H, d, $J$ = 10.2 Hz, $H_a$-9), 3.69 (1H, d, $J$ = 10.2 Hz, $H_b$-9), 2.88 (1H, d, $J$ = 14.7 Hz, $H_a$-5), 2.43 (1H, d, $J$ = 15.9 Hz, $^aCH_2$), 2.28 (1H, d, $J$ = 15.9 Hz, $^bCH_2$), 1.84 (1H, d, $J$ = 14.7 Hz, $H_b$-5), 1.63 (3H, s, Me), 1.21 (3H, s, Me); $^{13}$C NMR ($CDCl_3$)

$\delta$ = 174.8 (C=O), 142.1, 140.9, (arom C), 128.2, 127.7, 127.6, 127.1, 125.6, 125.1, (arom CH), 103.1 (C-1), 84.9 (quart C), 82.3 (C-4), 70.3 ($CH_2$), 44.8 (C-6), 43.6, 36.8 ($CH_2$), 31.7, 27.5 (Me). *Anal.* Calcd for $C_{22}H_{24}O_7$•1/3$H_2O$: C, 65.01; H, 6.12. Found: C, 65.12; H, 6.06.

**6-[2-Hydroperoxy-2-(4-methylphenyl)propyl]-1-hydroxy-4-(4-methylphenyl)-4-methyl-2,3,8-trioxabicyclo[4.3.0]nonan-7-one (3i):** Yield (124.3 mg, 58%); $R_f$ = 0.35 (EtOAc/hexane 4:6 v/v); colorless microcrystals (from $CHCl_3$/hexane); mp 209-211 °C; IR (KBr) $\nu$ 3600-3100 (OOH, OH), 1766 (C=O); $^1$H NMR ($CDCl_3$) $\delta$ = 8.84 (1H, s, OOH), 7.26-7.05 (8H, m, arom H), 4.37 (1H, d, $J$ = 10.8 Hz, $H_a$-9), 4.11 (1H, s, OH), 3.77 (1H, d, $J$ = 10.8 Hz, $H_b$-9), 3.03 (1H, d, $J$ = 14.7 Hz, $H_a$-5), 2.33 (8H, m, 2$CH_3$, 1H ($H_b$-5), 1H ($^a$$CH_2$)), 1.96 (1H, d, $J$ = 14.7 Hz, $^b$$CH_2$), 1.68, (3H, s, Me), 1.30 (3H, s, Me); $^{13}$C NMR ($CDCl_3$) $\delta$ = 174.7 (C=O), 138.9, 137.9, 137.3, 136.7, (arom C), 128.9, 128.5, 125.6, 125.0, (arom CH), 103.2 (C-1), 84.9 (quart C), 82.3 (C-4), 70.3 ($CH_2$), 44.7 (C-6), 43.6, 37.1 ($CH_2$), 31.8, 27.7, 21.1, 20.9 (Me). *Anal.* Calcd for $C_{24}H_{28}O_7$•4/5$H_2O$: C, 65.09; H, 6.74. Found: C, 64.72; H, 6.46.

**Reaction of 3-Substituted Tetronic Acids 1b-g with Various Alkenes 2a-l.** To a solution of the 3-substituted tetronic acid **1** (1 mmol) and alkene **2** (1 mmol) in glacial acetic acid (20 mL), manganese(III) acetate dehydrate (0.2 mmol) was added. The mixture was stirred at rt in air until the alkene **2** was completely consumed, and then the reaction was quenched by adding water (20 mL) to the mixture. The aqueous reaction mixture was extracted three times with $CH_2Cl_2$ (30 mL) and the combined extracts were washed with water, then a saturated aqueous solution of $NaHCO_3$, dried over anhydrous $MgSO_4$, and concentrated to dryness. The residue was purified by silica gel column chromatography while eluting with the appropriate solvent. The results are shown in Table 2.

**4,4-Bis(4-chlorophenyl)-1-hydroxy-6-methyl-2,3,8-trioxabicyclo[4.3.0]nonan-7-one (4ba):** Yield (329.1 mg, 83%); $R_f$ = 0.32 (EtOAc/hexane 4:7 v/v); colorless needles (from $CHCl_3$/hexane); mp 222-223 °C; IR (KBr) $\nu$ 3550-3150 (OH), 1762 (C=O); $^1$H NMR (DMSO-$d_6$) $\delta$ = 8.03 (1H, s, OH), 7.55-7.32 (8H, m, arom H), 4.25 (1H, d, $J$ = 10.5 Hz, $H_a$-9), 3.97 (1H, d, $J$ = 10.5 Hz, $H_b$-9), 3.40 (1H, d, $J$ = 14.4 Hz, $H_a$-5), 2.39 (1H, d, $J$ = 14.4 Hz, $H_b$-5), 1.25 (3H, s, Me); $^{13}$C NMR (DMSO-$d_6$) $\delta$ = 176.7 (C=O), 142.9, 139.3, 132.5, 131.74 (arom C), 128.8 (2C), 128.3 (2C), 127.6 (2C), 127.0 (2C), (arom CH), 100.2 (C-1), 83.7 (C-4), 70.4 ($CH_2$), 42.5 (C-6), 35.5 ($CH_2$), 20.9 (Me). *Anal.* Calcd for $C_{19}H_{16}Cl_2O_5$: C,57.74; H, 4.08. Found: C, 57.57; H, 4.26.

**4,4-Bis(4-fluorophenyl)-1-hydroxy-6-methyl-2,3,8-trioxabicyclo[4.3.0]nonan-7-one (4bb):** Yield (304.4 mg, 84%); $R_f$ = 0.49 (EtOAc/hexane 4:6 v/v); colorless needles (from $CHCl_3$/hexane); mp 210-211 °C; IR (KBr) $\nu$ 3550-3200 (OH), 1762 (C=O); $^1$H NMR (DMSO-$d_6$) $\delta$ = 8.03 (1H, s, OH), 7.57-7.07 (8H, m, arom H), 4.24 (1H, d, $J$ = 10.5 Hz, $H_a$-9), 3.96 (1H, d, $J$ = 10.5 Hz, $H_b$-9), 3.39 (1H, d, $J$ = 14.4 Hz, $H_a$-5), 2.41 (1H, d, $J$ = 14.4 Hz, $H_b$-5), 1.25 (3H, s, Me); $^{13}$C NMR (DMSO-$d_6$) $\delta$ = 176.8 (C=O), 162.7, 159.5, 140.7, 136.6 (arom C), 129.2 (1C), 129.1 (2C), 127.6 (1C), 127.5 (1C), 115.3 (1C),

115.0 (1C), 114.6 (1C), 114.3 (1C) (arom CH), 103.2 (C-1), 83.9 (C-4), 70.5 ($CH_2$), 42.6 (C-6), 35.9 ($CH_2$), 21.1 (Me). *Anal.* Calcd for $C_{19}H_{16}F_2O_5$: C, 62.98; H, 4.45. Found: C, 62.95; H, 4.61.

**1-Hydroxy-6-methyl-4,4-diphenyl-2,3,8-trioxabicyclo[4.3.0]nonan-7-one (4bc):** Yield (310 mg, 95%); $R_f$ = 0.51 ($Et_2O$/hexane 7:3 v/v); colorless needles (from $CHCl_3$/hexane); mp 205 °C; IR (KBr) $\nu$ 3550-3150 (OH), 1762 (C=O); $^1$H NMR (DMSO-$d_6$) $\delta$ = 7.96 (1H, s, OH), 7.53-7.15 (10H, m, arom H), 4.22 (1H, d, $J$ = 10.5 Hz, $H_a$-9), 3.95 (1H, d, $J$ = 10.5 Hz, $H_b$-9), 3.41 (1H, d, $J$ = 14.4 Hz, $H_a$-5), 2.40 (1H, d, $J$ = 14.4 Hz, $H_b$-5), 1.24 (3H, s, Me); $^{13}$C NMR (DMSO-$d_6$) $\delta$ = 176.8 (C=O), 144.8, 140.8 (arom C), 128.2 (2C), 127.6 (1C), 127.5 (1C), 126.7 (2C), 124.9 (2C) (arom CH), 103.1 (C-1), 84.3 (C-4), 70.5 ($CH_2$), 42.4 (C-6), 35.8 ($CH_2$), 21.1 (Me). *Anal.* Calcd for $C_{19}H_{18}O_5$: C, 69.93; H, 5.56. Found: C, 69.69; H, 5.55.

**1-Hydroxy-4,4-bis(4-methylphenyl)-6-methyl-2,3,8-trioxabicyclo[4.3.0]nonan-7-one (4bd):** Yield (294.2 mg, 83%); $R_f$ = 0.54 (EtOAc/hexane 3:7 v/v); colorless needles (from $CHCl_3$/hexane); mp 209-210 °C; IR (KBr) $\nu$ 3550-3200 (OH), 1762 (C=O); $^1$H NMR (DMSO-$d_6$) $\delta$ = 7.88 (1H, s, OH), 7.35-7.02 (8H, m, arom H), 4.19 (1H, d, $J$ = 10.5 Hz, $H_a$-9), 3.91 (1H, d, $J$ = 10.5 Hz, $H_b$-9), 3.28 (1H, d, $J$ = 14.4 Hz, $H_a$-5), 2.35 (1H, d, $J$ = 14.4 Hz, $H_b$-5), 2.22 (3H, s, Me), 2.20 (3H, s, Me), 1.22 (3H, s, Me); $^{13}$C NMR (DMSO-$d_6$) $\delta$ = 176.9 (C=O), 142.1, 137.9, 136.8, 135.7 (arom C), 128.7 (2C), 128.2 (2C), 126.8 (2C), 125.1 (2C) (arom CH), 102.9 (C-1), 84.3 (C-4), 70.6 ($CH_2$), 42.5 (C-6), 35.9 ($CH_2$), 21.2, 20.6, 20.5 (Me). *Anal.* Calcd for $C_{21}H_{22}O_5$: C, 71.17; H, 6.26. Found: C, 70.88; H, 6.37.

**1-Hydroxy-4,4-bis(4-methoxyphenyl)-6-methyl-2,3,8-trioxabicyclo[4.3.0]nonan-7-one (4be):** Yield (309.1 mg, 80%); $R_f$ = 0.32 (EtOAc/hexane 4:7 v/v); colorless needles (from EtOAc/hexane); mp 173-174 °C; IR (KBr) $\nu$ 3500-3200 (OH), 1743 (C=O); $^1$H NMR (DMSO-$d_6$) $\delta$ = 7.91 (1H, s, OH), 7.38-6.79 (8H, m, arom H), 4.20 (1H, d, $J$ = 10.8 Hz, $H_a$-9), 3.92 (1H, d, $J$ = 10.8 Hz, $H_b$-9), 3.24 (1H, d, $J$ = 14.7 Hz, $H_a$-5), 3.72(3H, s, Me), 3.69(3H, s, Me), 2.38 (1H, d, $J$ = 14.7 Hz, $H_b$-5), 1.23 (3H, s, Me); $^{13}$C NMR (DMSO-$d_6$) $\delta$ = 176.9 (C=O), 158.5, 157.9, 137.1, 132.7 (arom C), 128.3 (2C), 126.9 (2C), 113.5 (2C), 112.9 (2C) (arom CH), 102.9 (C-1), 84.2 (C-4), 70.6 ($CH_2$), 42.5 (C-6), 55.1, 54.9 MeO), 36.1 ($CH_2$), 21.3 (Me). *Anal.* Calcd for $C_{21}H_{22}O_7$: C, 65.28; H, 5.74. Found: C, 65.25; H, 5.97.

**4-(4-Bromophenyl)-4-(4-chlorophenyl)-1-hydroxy-6-methyl-2,3,8-trioxabicyclo[4.3.0]nonan-7-one (4bf):** Yield (382.5 mg, 87%); $R_f$ = 0.56 (EtOAc/hexane 3:7 v/v); colorless needles (from EtOAc/hexane), mp 229-231 °C; IR (KBr) $\nu$ 3500-3200 (OH), 1762 (C=O); $^1$H NMR (DMSO-$d_6$) $\delta$ = 8.06 (1H, s, OH), 8.05-7.32 (4H, m, arom H), 4.25 (1H, d, $J$ = 6.6 Hz, $H_a$-9), 3.95 (1H, d, $J$ = 6.6 Hz, $H_b$-9), 3.38 (1H, d, $J$ = 8.7 Hz, $H_a$-5), 2.38 (1H, d, $J$ = 8.7 Hz, $H_b$-5), 1.24 (3H, s, Me); $^{13}$C NMR (DMSO-$d_6$) $\delta$ = 176.8 (C=O), 143.4, 142.9, 139.8, 139.4 (arom C), 131.4, 130.7, 129.2, 128.9, 128.4, 127.7, 127.4, 127.1 (arom CH), 103.3 (C-1), 83.9 (C-4), 70.5 ($CH_2$), 42.5 (C-6), 35.5 ($CH_2$), 20.9 (Me). *Anal.* Calcd for $C_{19}H_{16}BrClO_5$: C, 51.90; H, 3.67. Found: C, 51.70; H, 3.69.

**4-(4-Chlorophenyl)-1-hydroxy-4,6-dimethyl-2,3,8-trioxabicyclo[4.3.0]nonan-7-one (4bg):** Yield (254.2 mg, 85%); *dr* = 81:19.

**Major Diastereomer:** $R_f$ = 0.62 (EtOAc/hexane 4:6 v/v); colorless blocks (from $CHCl_3$/hexane); mp 206 °C; IR (KBr) $\nu$ 3500-3100 (OH), 1726 (C=O); $^1$H NMR ($CDCl_3$) $\delta$ = 7.40-7.26 (4H, m, arom H), 4.13 (1H, d, $J$ = 6.3 Hz, $H_a$-9), 3.93 (1H, d, $J$ = 6.3 Hz, $H_b$-9), 3.81 (1H, s, OH), 3.00 (1H, d, $J$ = 8.7 Hz, $H_a$-5), 1.98 (1H, d, $J$ = 8.7 Hz, $H_b$-5), 1.37 (3H, s, Me), 1.31 (3H, s, Me); $^{13}$C NMR ($CDCl_3$) $\delta$ = 176.7 (C=O), 139.4, 133.2 (arom C), 128.2 (2C), 127.4(2C), (arom CH), 103.2 (C-1), 82.3 (C-4), 70.3 ($CH_2$), 42.3 (C-6), 36.5 ($CH_2$), 31.4, 21.7 (Me). *Anal.* Calcd for $C_{14}H_{15}ClO_5$: C, 56.29; H, 5.06. Found: C, 56.00; H, 5.02.

**Minor Diastereomer**: $R_f$ = 0.81 (EtOAc/hexane 4:6 v/v); colorless needles (from $CHCl_3$/hexane); mp 185-187 °C; IR (KBr) $\nu$ 3500-3200 (OH), 1764 (C=O); $^1$H NMR ($CDCl_3$) $\delta$ = 7.36-7.26 (4H, m, arom H), 4.31 (1H, d, $J$ = 6.3 Hz, $H_a$-9), 4.24 (1H, d, $J$ = 6.3 Hz, $H_b$-9), 3.58 (1H, s, OH), 2.63 (1H, d, $J$ = 8.4 Hz, $H_a$-5), 2.04 (1H, d, $J$ = 8.4 Hz, $H_b$-5), 1.61 (3H, s, Me), 1.57 (3H, s, Me); $^{13}$C NMR ($CDCl_3$) 178.0 (C=O), 142.9, 134.1 (arom C), 128.7 (2C), 125.6 (2C) (arom CH), 103.7 (C-1), 81.1 (C-4), 70.7 ($CH_2$), 42.6 (C-6), 38.4 ($CH_2$), 24.7, 21.4 (Me). *Anal.* Calcd for $C_{14}H_{15}ClO_5$: C, 56.29; H, 5.06. Found: C, 55.99; H, 5.05.

**1-Hydroxy-4,6-dimethyl-4-phenyl-2,3,8-trioxabicyclo[4.3.0]nonan-7-one (4bh):** Yield (256.3 mg, 97%); *dr* = 54:46.

**Major Diastereomer:** $R_f$ = 0.26 (EtOAc/hexane 3:7 v/v); colorless needles (from $CHCl_3$/hexane); mp 177-178 °C; IR (KBr) $\nu$ 3500-3100 (OH), 1766 (C=O); $^1$H NMR ($CDCl_3$) $\delta$ = 7.39-7.16 (5H, m, arom H), 4.04 (1H, d, $J$ = 10.5 Hz, $H_a$-9), 3.85 (1H, d, $J$ = 10.5 Hz, $H_b$-9), 3.68 (1H, s, OH), 2.99 (1H, d, $J$ = 14.4 Hz, $H_a$-5), 1.91 (1H, d, $J$ = 14.4 Hz, $H_b$-5), 1.33 (3H, s, Me), 1.24 (3H, s, Me); $^{13}$C NMR ($CDCl_3$) $\delta$ = 176.7 (C=O), 140.8 (arom C), 127.9 (2C), 127.3 (1C), 125.8 (2C) (arom CH), 103.1 (C-1), 82.7 (C-4), 70.3 ($CH_2$), 42.4 (C-6), 36.7 ($CH_2$), 31.5, 21.8 (Me). *Anal.* Calcd for $C_{14}H_{16}O_5$: C, 63.63; H, 6.10. Found: C, 63.47; H, 6.08.

**Minor Diastereomer:** $R_f$ = 0.45 (EtOAc/hexane 3:7 v/v); colorless blocks (from $CHCl_3$/hexane), mp 168-170 °C; IR (KBr) $\nu$ 3500-3200 (OH), 1762 (C=O); $^1$H NMR ($CDCl_3$) $\delta$ = 7.29-7.19 (5H, m, arom H), 4.22 (1H, d, $J$ = 10.2 Hz, $H_a$-9), 4.14 (1H, d, $J$ = 10.2 Hz, $H_b$-9), 3.69 (1H, s, OH), 2.57 (1H, d, $J$ = 14.1 Hz, $H_a$-5), 2.02 (1H, d, $J$ = 14.1 Hz, $H_b$-5), 1.51 (3H, s, Me), 1.22 (3H, s, Me); $^{13}$C NMR ($CDCl_3$) $\delta$ = 178.4 (C=O), 144.4 (arom C), 128.6 (2C), 127.9 (1C), 124.0 (2C) (arom CH), 103.7 (C-1), 81.4 (C-4), 70.7 ($CH_2$), 42.7 (C-6), 38.3 ($CH_2$), 24.8, 21.4 (Me). *Anal.* Calcd for $C_{14}H_{16}O_5$•1/8 $H_2O$: C, 63.09; H, 6.15. Found: C, 63.23; H, 6.31.

**1-Hydroxy-4-(4-methylphenyl)-4,6-dimethyl-2,3,8-trioxabicyclo[4.3.0]nonan-7-one (4bi):** Yield (235.6 mg, 84%); *dr* = 50:50.

**Diastereomer:** $R_f$ = 0.52 (EtOAc/hexane 3:7 v/v); colorless microcrystals (from $CHCl_3$/hexane); mp 172 °C; IR (KBr) $\nu$ 3550-3200 (OH), 1759 (C=O); $^1$H NMR ($CDCl_3$) $\delta$ = 7.26-7.15 (4H, m, arom H), 4.26 (1H, d, $J$ = 6.6 Hz, $H_a$-9), 4.25 (1H, s, OH), 4.19 (1H, d, $J$ = 6.6 Hz, $H_b$-9), 2.58 (1H, d, $J$ = 8.7 Hz, $H_a$-5), 2.33 (3H, s, Me), 2.08 (1H, d, $J$ = 8.7 Hz, $H_b$-5), 1.55 (3H, s, Me), 1.27 (3H, s, Me); $^{13}$C NMR ($CDCl_3$) $\delta$ = 178.6 (C=O), 141.4, 137.7 (arom C), 129.1 (2C), 124.1 (2C) (arom CH), 103.5 (C-1), 81.2 (C-4), 70.8 ($CH_2$), 42.7 (C-6), 38.3 ($CH_2$), 24.6, 21.3, 20.9 (Me). *Anal.* Calcd for $C_{15}H_{18}O_5$: C, 64.74; H, 6.52. Found: C, 64.50; H, 6.50.

**The Other Diastereomer:** $R_f$ = 0.36 (EtOAc/hexane 3:7 v/v); colorless needles (from $CHCl_3$/hexane); mp 198-199 °C; IR (KBr) $\nu$ 3500-3100 (OH), 1759 (C=O); $^1$H NMR ($CDCl_3$) $\delta$ = 7.34-7.12 (4H, m, arom H), 4.11 (1H, d, $J$ = 6.6 Hz, $H_a$-9), 3.92 (1H, d, $J$ = 6.6 Hz, $H_b$-9), 3.76 (1H, s, OH), 3.05 (1H, d, $J$ = 8.7 Hz, $H_a$-5), 2.31 (3H, s, Me), 1.96 (1H, d, $J$ = 8.7 Hz, $H_b$-5), 1.38 (3H, s, Me), 1.31 (3H, s, Me); $^{13}$C NMR ($CDCl_3$) $\delta$ = 176.8 (C=O), 137.8, 136.8 (arom C), 128.7 (2C), 125.7 (2C) (arom CH), 103.1 (C-1), 82.6 (C-4), 70.3 ($CH_2$), 42.3 (C-6), 36.6 ($CH_2$), 31.6, 21.8, 21.0 (Me). *Anal.* Calcd for $C_{15}H_{18}O_5$•1/6$H_2O$: C, 64.05; H, 6.57. Found: C, 64.20; H, 6.43.

**1-Hydroxy-6-methyl-4-phenyl-4-(2-thienyl)-2,3,8-trioxabicyclo[4.3.0]nonan-7-one (4bk):** Yield (255.9 mg, 77%); *dr* = 54:46.

M**ajor Diastereomer:** $R_f$ = 0.42 (EtOAc/hexane 3:7 v/v); colorless cubes (from $CHCl_3$/hexane); mp 154-156 °C; IR (KBr) $\nu$ 3600-3200 (OH), 1772 (C=O); $^1$H NMR ($CDCl_3$) $\delta$ = 7.52-6.66 (9H, m, arom H, thienyl H), 4.08 (1H, d, $J$ = 10.5 Hz, $CH_2^a$), 3.90 (1H, d, $J$ = 10.5 Hz, $CH_2^b$), 3.62 (1H, s, OH), 3.32 (1H, d, $J$ = 14.7 Hz, $H_a$-5), 2.54 (1H, d, $J$ = 14.7 Hz, $H_b$-5), 1.31(3H, s, Me); $^{13}$C NMR ($CDCl_3$) $\delta$ = 176.3 (C=O), 146.5 (arom C), 138.5 (thienyl C), 128.2, 127.8, 127.2, 127.1, 126.7 (arom CH, thienyl CH), 103.4 (C-1), 83.9 (C-4), 70.2 ($CH_2$), 42.9 (C-6), 37.6 ($CH_2$), 21.8 (Me). *Anal.* Calcd for $C_{17}H_{16}O_5S$•1/4$H_2O$: C, 60.61; H, 4.94. Found: C, 60.73; H, 4.69.

**Minor Diastereomer:** $R_f$ = 0.46 (EtOAc/hexane 3:7 v/v); colorless needles (from $CHCl_3$/hexane); mp 158-160 °C; IR (KBr) $\nu$ 3550-3200 (OH), 1755 (C=O); $^1$H NMR ($CDCl_3$) $\delta$ = 7.31-6.91 (9H, m, arom H, thienyl H), 4.22 (1H, d, $J$ = 10.5 Hz, $H_a$-9), 4.07 (1H, d, $J$ = 10.5 Hz, $H_b$-9), 3.57 (1H, s, OH), 3.32 (1H, d, $J$ = 14.7 Hz, $H_a$-5), 2.40 (1H, d, $J$ = 14.7 Hz, $H_b$-5), 1.36 (3H, s, Me); $^{13}$C NMR ($CDCl_3$) $\delta$ = 177.2 (C=O), 144.4 (arom C), 143.9 (thienyl C), 128.5, 128.3, 127.4, 126.6, 126.2, 124.8 (arom CH, thienyl CH), 103.5 (C-1), 84.3 ( C-4), 70.6 ($CH_2$), 42.6 (C-6), 38.3 ($CH_2$), 21.9 (Me). *Anal.* Calcd for $C_{17}H_{16}O_5S$•2/3$H_2O$: C, 59.29; H, 5.07. Found: C, 59.17; H, 5.26.

**1-Hydroxy-6-methyl-4-phenyl-2,3,8-trioxabicyclo[4.3.0]nonan-7-one (4bl):** Yield (235.2 mg, 94%); *dr* = 50:50).

**Diastereomer:** $R_f$ = 0.42 (EtOAc/hexane 3:7 v/v); colorless microcrystals (from $CHCl_3$/hexane); mp 157 °C; IR (KBr) $\nu$ 3550-3100 (OH), 1751 (C=O); $^1$H NMR ($CDCl_3$) $\delta$ = 7.39-7.26 (5H, m, arom H),

5.26 (1H, t, *J* = 6.3 Hz, CH), 4.27 (1H, d, *J* = 10.2 Hz, $H_a$-9), 4.23 (1H, d, *J* = 10.2 Hz, $H_b$-9), 3.97 (1H, s, OH), 2.48 (1H, dd, *J* = 15.0, 6.3 Hz, $H_a$-5), 2.36 (1H, dd, *J* = 15.0, 6.3 Hz, $H_b$-5), 1.42 (3H, s, Me); $^{13}$C NMR ($CDCl_3$) $\delta$ = 177.6 (C=O), 137.8 (arom C), 128.5 (2C), 128.2 (1C), 126.1 (2C) (arom CH), 104.5 (C-1), 78.4 (CH, C-4), 71.8 ($CH_2$), 42.3 (C-6), 33.5 ($CH_2$), 17.8 (Me). *Anal.* Calcd for $C_{13}H_{14}O_5$•1/4$H_2O$: C, 61.29; H, 5.74. Found: C, 61.48; H, 5.72.

**The Other Diastereomer:** $R_f$ = 0.39 (EtOAc/hexane 3:7 v/v); colorless microcrystals (from $CHCl_3$/hexane); mp 148-149 °C; IR (KBr) $\nu$ 3550-3100 (OH), 1751 (C=O); $^1$H NMR ($CDCl_3$) $\delta$ = 7.29-7.19 (5H, m, arom H), 4.99 (1H, dd, *J* = 12.0, 2.4 Hz, CH), 4.21 (1H, d, *J* = 10.4 Hz, $H_a$-9), 4.01 (1H, d, *J* = 10.4 Hz, $H_b$-9), 3.87 (1H, s, OH), 2.41 (1H, dd, *J* = 12.0. 2.4 Hz, $H_a$-5), 2.00 (1H, dd, *J* = 12.0, 12.0 Hz, $H_b$-5), 1.29 (3H, s, Me); $^{13}$C NMR ($CDCl_3$) $\delta$ = 177.4 (C=O), 136.4 (arom C), 129.2 (1C), 128.7(2C), 126.9(2C) (arom CH), 103.8 (C-1), 81.1 (CH, C-4), 69.9 ($CH_2$), 44.1 (C-6), 34.1 ($CH_2$), 20.5 (Me). *Anal.* Calcd for $C_{13}H_{14}O_5$•1/6$H_2O$: C, 61.65; H, 5.70. Found: C, 61.95; H, 5.60.

**6-Ethyl-1-hydroxy-4,4-diphenyl-2,3,8-trioxabicyclo[4.3.0]nonan-7-one (4cc):** Yield (279.1 mg, 82%); $R_f$ = 0.51 (EtOAc/hexane 3:7 v/v); colorless blocks (from $CHCl_3$/hexane); mp 208 °C; IR (KBr) $\nu$ 3550-3200 (OH), 1759 (C=O); $^1$H NMR (DMSO-$d_6$) $\delta$ = 7.95 (1H, s, OH), 7.53-7.13 (10H, m, arom H), 4.15 (1H, d, *J* = 10.8 Hz, $H_a$-9), 3.93 (1H, d, *J* = 10.8 Hz, $H_b$-9), 3.44 (1H, d, *J* = 14.1 Hz, $H_a$-5), 2.31 (1H, d, *J* = 14.1 Hz, $H_b$-5), 1.72 (2H, m, $CH_2$), 0.93 (3H, t, *J* = 7.2 Hz, Me); $^{13}$C NMR (DMSO-$d_6$) $\delta$ = 175.4 (C=O), 145.2, 141.0 (arom C), 128.3 (2C), 127.6 (2C), 127.5 (2C), 126.8 (2C), 125.0 (2C) (arom CH), 103.2 (C-1), 84.4 (C-4), 71.2 ($CH_2$), 45.9 (C-6), 34.6, 27.9 ($CH_2$), 7.8 (Me). *Anal.* Calcd for $C_{20}H_{20}O_5$: C, 70.57; H, 5.92. Found: C, 70.39; H, 5.72.

**1-Hydroxy-6-isopropyl-4,4-diphenyl-2,3,8-trioxabicyclo[4.3.0]nonan-7-one (4dc):** Yield (276.4 mg, 78%); $R_f$ = 0.58 (EtOAc/hexane 3:7 v/v); colorless blocks (from EtOAc/hexane); mp 227-228 °C; IR (KBr) $\nu$ 3500-3200 (OH), 1751 (C=O); $^1$H NMR (DMSO-$d_6$) $\delta$ = 7.99 (1H, s, OH), 7.48-7.14 (10H, m, arom H), 4.11 (1H, d, *J* = 6.6 Hz, $H_a$-9), 3.47 (1H, d, *J* = 8.4 Hz, $H_a$-5), 3.36 (1H, d, *J* = 6.6 Hz, $H_b$-9), 2.33 (1H, d, *J* = 8.4 Hz, $H_b$-5), 2.08 (1H, m, CH), 1.07 (3H, d, *J* = 4.2 Hz, Me), 0.95 (3H, d, *J* = 4.2 Hz, Me); $^{13}$C NMR (DMSO-$d_6$) $\delta$ = 174.7 (C=O), 145.8, 141.33 (arom C), 128.3 (2C), 127.7 (2C), 127.4 (1C), 126.8 (1C), 126.4 (1C), 124.9 (2C) (arom CH), 103.7 (C-1), 84.4 (C-4), 72.88 ($CH_2$), 48.8 (C-6), 35.8 ($CH_2$), 33.7 (CH), 18.8, 17.3 (Me). *Anal.* Calcd for $C_{21}H_{22}O_5$: C, 71.17; H, 6.26. Found: C, 71.12; H, 6.14.

**6-Butyl-1-hydroxy-4,4-diphenyl-2,3,8-trioxabicyclo[4.3.0]nonan-7-one (4ec):** Yield (261.6 mg, 71%); $R_f$ = 0.56 (EtOAc/hexane 3:7 v/v); colorless needles (from $CHCl_3$/hexane); mp 184 °C; IR (KBr) $\nu$ 3550-3200 (OH), 1759 (C=O); $^1$H NMR ($CDCl_3$) $\delta$ = 7.47-7.11 (10H, m, arom H), 4.18 (1H, s, OH), 3.99 (1H, d, *J* = 10.8 Hz, $H_a$-9), 3.76 (1H, d, *J* = 10.8 Hz, $H_b$-9), 3.33 (1H, d, *J* = 14.4 Hz, $H_a$-5), 2.28 (1H, d, *J* = 14.4 Hz, $H_b$-5), 1.64-1.57 (2H, m, $CH_2$), 1.40-1.15 (4H, m, 2$CH_2$), 0.83 (3H, t, *J* = 7.2 Hz, Me); $^{13}$C

NMR ($CDCl_3$) $\delta$ = 176.1 (C=O), 144.3, 139.4 (arom C), 128.4, 128.3, 127.9, 127.9, 127.4, 127.1, 125.2 (arom CH), 103.3 (C-1), 85.5 (C-4), 70.9 ($CH_2$), 45.9 (C-6), 35.9, 35.7, 25.2, 22.9 ($CH_2$), 13.8 (Me). *Anal.* Calcd for $C_{22}H_{24}O_5$: C, 71.72; H, 6.57. Found: C, 71.69; H, 6.37.

**6-Benzyl-1-hydroxy-4,4-diphenyl-2,3,8-trioxabicyclo[4.3.0]nonan-7-one (4fc):** Yield (321.94 mg, 80%), $R_f$ = 0.33 (EtOAc/hexane 2:8 v/v); colorless needles (from $CHCl_3$/hexane); mp 215 °C; IR (KBr) $\nu$ 3500-3200 (OH), 1739 (C=O); $^1$H NMR (DMSO-$d_6$) $\delta$ = 8.24 (1H, s, OH), 7.48-7.15 (15H, m, arom H), 3.73 (1H, d, $J$ = 10.8 Hz, $H_a$-9), 3.39 (1H, d, $J$ = 10.8 Hz, $H_b$-9), 3.34 (1H, d, $J$ = 14.1 Hz, $H_a$-5), 3.12 (1H, d, $J$ = 13.5 Hz, $CH_2$), 2.88 (1H, d, $J$ = 13.5 Hz, $CH_2$), 2.56 (1H, d, $J$ = 14.1 Hz, $H_b$-5); $^{13}$C NMR (DMSO-$d_6$) $\delta$ = 175.2 (C=O), 145.0, 141.0, 135.1 (arom C), 130.6, 128.4, 128.0, 127.6, 127.2, 126.8, 126.7, 125.0 (arom CH), 102.8 (C-1), 84.5 (C-4), 70.7 ($CH_2$), 48.1 (C-6), 40.9, 35.6 ($CH_2$). *Anal.* Calcd for $C_{25}H_{22}O_5$: C, 74.61; H, 5.51. Found: C, 74.31; H, 5.55.

**4,4-Bis(4-chlorophenyl)-1-hydroxy-6-pentyl-2,3,8-trioxabicyclo[4.3.0]nonan-7-one (4ga):** Yield (401.7 mg, 89%); $R_f$ = 0.94 (EtOAc/hexane 4:6 v/v); colorless needles (from $CHCl_3$/hexane); mp 188 °C; IR (KBr) $\nu$ 3550-3200 (OH), 1747 (C=O); $^1$H NMR ($CDCl_3$) $\delta$ = 7.47-7.12 (8H, m, arom H), 4.14 (1H, d, $J$ = 10.5 Hz, $H_a$-9), 3.93 (1H, d, $J$ = 10.5 Hz, $H_b$-9), 3.87 (1H, s, OH), 3.34 (1H, d, $J$ = 14.7 Hz, $H_a$-5), 2.29 (1H, d, $J$ = 14.7 Hz, $H_b$-5), 1.72-1.66 (2H, m, $CH_2$), 1.37-1.23 (6H, m, $3CH_2$), 0.88 (3H, t, $J$ = 7.2 Hz, Me); $^{13}$C NMR ($CDCl_3$) $\delta$ = 175.8 (C=O), 142.3, 137.6, 134.1, 133.7 (arom C), 128.7, 128.6, 128.4, 126.6 (arom CH), 103.4 (C-1), 84.9 (C-4), 71.0 ($CH_2$), 46.0 (C-6), 36.0, 35.5, 31.9, 22.8, 22.3 ($CH_2$), 13.9 (Me). *Anal.* Calcd for $C_{23}H_{24}Cl_2O_5$•1/2$H_2O$: C, 60.01; H, 5.47. Found: C, 60.18; H, 5.22.

**Reaction at Elevated Temperature.** The 1,1-diarylethene **2a** or **2c** (0.5 mmol) was placed in a 100 mL volumetric flask with a magnetic stirrer. Glacial acetic acid (20 mL) and the tetronic acid derivatives **1a-g** (2 mmol) were added to the flask. Manganese(III) acetate (2 mmol) was then added to the mixture. The flask was installed an argon balloon and degassing in the flask was performed under reduced pressure using an ultrasonic bath for 15 minutes. For the tetronic acid (**1a**), the reaction was carried out in air (Table 3, Entries 1 and 2). The mixture was then heated under reflux until the dark-brown color of manganese(III) disappeared. After reaction, the acetic acid was removed in vacuo and the residue was triturated with water (25 mL) followed by extraction three times with $CH_2Cl_2$ (30 mL). The combined extracts were washed with water (30 mL) followed by saturated aqueous $NaHCO_3$ solution (30 mL), dried over anhydrous $MgSO_4$, filtered and then concentrated to dryness. The products were separated by silica gel column chromatography while eluting with EtOAc/hexane 3:7 v/v. The results are shown in Table 3.

**3,3-Bis[2-acetoxy-2,2-bis(4-chlorophenyl)ethyl]tetrahydrofuran-2,4-dione (5aa):** Yield (229 mg, 32%); $R_f$ = 0.49 (EtOAc/hexane 4:6 v/v); colorless microcrystals (from $CHCl_3$); mp 155-156 °C; IR (KBr) $\nu$ 1807, 1759 (C=O); $^1$H NMR ($CDCl_3$) $\delta$ = 7.26-7.09 (16H, m, arom H), 3.65 (2H, d, $J$ = 8.7 Hz, $CH_2$), 3.52 (2H, s, $CH_2$), 3.42 (2H, d, $J$ = 8.7 Hz, $CH_2$), 2.04 (6H, s, 2OAc); $^{13}$C NMR ($CDCl_3$) $\delta$ = 208.2,

173.7, 168.9 (C=O), 141.2, 140.9, 134.0, 133.9 (arom C), 128.6, 128.5, 127.7, 126.9 (arom CH), 82.0 (quart C), 72.8 ($CH_2$), 46.8 (C-3), 44.1 ($CH_2$), 22.1 (Me). FAB HRMS (acetone/NBA/NaI) calcd for $C_{36}H_{28}{}^{35}Cl_4O_7Na$ 735.0487 (M+Na). Found 735.0468.

**3,3-Bis(2-acetoxy-2,2-diphenylethyl)tetrahydrofuran-2,4-dione (5ac):** Yield (184 mg, 20%); $R_f$ = 0.49 (EtOAc/hexane 4:6 v/v); colorless microcrystals (from $CHCl_3$); mp 222-223 °C; IR (KBr) $\nu$ 1805, 1759 (C=O); $^1$H NMR ($CDCl_3$) $\delta$ = 7.26-7.18 (20H, m, arom H), 3.77 (2H, d, $J$ = 14.4 Hz, $CH_2$), 3.34 (2H, s, $CH_2$), 3.51 (2H, d, $J$ = 14.4 Hz, $CH_2$), 2.04 (6H, s, 2OAc); $^{13}$C NMR ($CDCl_3$) $\delta$ = 208.7, 174.1, 169.1 (C=O), 143.2, 142.7 (arom C), 128.2, 128.1, 127.6, 127.5,126.4, 125.6 (arom CH), 82.8 (quart C), 72.6 ($CH_2$), 46.9 (C-3), 44.8 ($CH_2$), 22.2 (Me). *Anal.* Calcd for $C_{36}H_{32}O_7$•1/3$H_2O$: C, 74.21; H, 5.65. Found: C, 74.48; H, 5.44.

**3-[2,2-Bis(4-chlorophenyl)ethenyl]-3-[2-acetoxy-2,2-bis(4-chlorophenyl)ethyl]-tetrahydrofuran-2,4-dione (6):** Yield (85 mg, 13%); $R_f$ = 0.49 (EtOAc/hexane 4:6 v/v); colorless microcrystals (from $CHCl_3$); mp 231-233 °C; IR (KBr) $\nu$ 1801, 1757 (C=O); $^1$H NMR ($CDCl_3$) $\delta$ = 7.39-6.92 (16H, m, arom H), 6.0 (1H, s, CH=), 3.95 (1H, d, $J$ = 8.4 Hz, $CH_2$), 3.70 (1H, d, $J$ = 8.4 Hz, $CH_2$), 3.54 (1H, d, $J$ = 9.9 Hz, $CH_2$), 2.93 (1H, d, $J$ = 9.9 Hz, $CH_2$), 2.08 (3H, s, OAc); $^{13}$C NMR ($CDCl_3$) $\delta$ = 208.2, 174.2, 168.9 (C=O), 144.7, 141.2, 140.7, 138.2, 135.3, 134.9, 134.7, 133.9 (arom C), 129.0, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.1, 127.6, 126.8, 126.5 (arom CH and CH=), 134.1 (quart C), 82.1 (quart C), 73.2 ($CH_2$), 50.4 (C-3), 43.9 ($CH_2$), 21.9 (Me). FAB HRMS (acetone/NBA/NaI) calcd for $C_{34}H_{24}{}^{35}Cl_4O_5Na$ 675.0276 (M+Na). Found 675.0320.

**4,4,11,11-Tetraphenyl-2,3,8,10-tetraoxatricyclo[4.3.3.0$^{1,6}$]tridecan-7-one (7):** Yield (59 mg, 12%); $R_f$ = 0.53 ($CHCl_3$); colorless needles (from $CHCl_3$/hexane); mp 203-205 °C; IR (KBr) $\nu$ 1774 (C=O); $^1$H NMR ($CDCl_3$) $\delta$ = 7.44-7.15 (20H, m, arom H), 4.41 (1H, d, $J$ = 10.2 Hz, $CH_2$), 4.32 (1H, d, $J$ = 10.2 Hz, $CH_2$), 3.26 (1H, d, $J$ = 14.4 Hz, $CH_2$), 3.10 (1H, d, $J$ = 13.5 Hz, $CH_2$), 2.82 (1H, d, $J$ = 13.5 Hz, $CH_2$), 2.64 (1H, d, $J$ = 14.4 Hz, $CH_2$); $^{13}$C NMR ($CDCl_3$) $\delta$ = 176.3 (C=O), 145.0, 144.1, 143.2, 142.5 (arom C), 128.9, 128.5, 128.4, 128.1, 127.8, 127.7, 127.5, 127.2, 125.9,125.8, 125.4, 125.3 (arom CH), 113.6, 91.6, 83.8 (quart C), 72.9 ($CH_2$), 50.9 (quart C), 44.0, 35.6 ($CH_2$). FAB HRMS (acetone/NBA/NaI) calcd for $C_{32}H_{26}O_5Na$ 513.1678 (M+Na). Found 513.1733.

**3-[2-Acetoxy-2,2-bis(4-chlorophenyl)ethyl]-3-methyltetrahydrofuran-2,4-dione (8ba):** Yield (125 mg, 60%); $R_f$ = 0.88 (EtOAc/hexane 4:6 v/v); colorless microcrystals (from $CHCl_3$); mp 191-192 °C; IR (KBr) $\nu$ 1801, 1755 (C=O); $^1$H NMR ($CDCl_3$) $\delta$ = 7.25-7.18 (8H, m, arom H), 4.33 (1H, d, $J$ = 10.5 Hz, $CH_2$), 3.83 (1H, d, $J$ = 10.5 Hz, $CH_2$), 3.69 (1H, d, $J$ = 8.7 Hz, $CH_2$), 3.31 (1H, d, $J$ = 8.7 Hz, $CH_2$), 2.12 (OAc), 1.34 (3H, s, Me); $^{13}$C NMR ($CDCl_3$) $\delta$ = 208.5, 175.8, 169.1 (C=O), 141.7, 141.0, 134.2, 133.9 (arom C), 128.6, 127.9, 127.2 (arom CH), 82.3 (quart C), 71.9, 41.4 ($CH_2$), 45.1 (C-3), 24.7, 22.2 (Me). *Anal.* Calcd for $C_{21}H_{18}Cl_2O_5$•1/3$H_2O$: C, 59.03; H, 4.40. Found: C, 59.16; H, 4.29.

**3-(2-Acetoxy-2,2-diphenylethyl)-3-methyltetrahydrofuran-2,4-dione (8bc):** Yield (56.4 mg, 32%); $R_f$ = 0.33 (EtOAc/hexane 3:7 v/v); colorless blocks (from $CHCl_3$/hexane); mp 193-194 °C; IR (KBr) $\nu$ 1805, 1757, 1739 (C=O); $^1$H NMR ($CDCl_3$) $\delta$ = 7.22-7.16 (10H, m, arom H), 4.16 (1H, d, $J$ = 16.8 Hz, $CH_2$), 3.69 (1H, , d, $J$ = 15.0 Hz, $CH_2$), 3.51 (1H, d, $J$ = 16.8 Hz, $CH_2$), ), 3.31 (1H, d, $J$ = 15.0 Hz, $CH_2$), 2.06 (3H, s, OAc), 1.26 (3H, s, Me); $^{13}$C NMR ($CDCl_3$) $\delta$ = 208.8, 176.1, 169.2 (C=O), 143.5, 142.8 (arom C), 128.3, 128.2, 127.9, 127.7, 126.5, 125.7 (arom CH), 83.1 (quart C), 71.7 ($CH_2$), 45.2 (C-3), 41.9 ($CH_2$), 24.6, 22.2 (Me). FAB HRMS (acetone/NBA/NaI) calcd for $C_{21}H_{20}O_5Na$ 375.1208 (M+Na). Found 375.1275.

**3-(2-Acetoxy-2,2-diphenylethyl)-3-ethyltetrahydrofuran-2,4-dione (8cc):** Yield (93 mg, 51%); $R_f$ = 0.49 (EtOAc/hexane 3:7 v/v); colorless microcrystals (from $CHCl_3$); mp 155-156 °C; IR ($CHCl_3$) $\nu$ 1803, 1755 (C=O); $^1$H NMR ($CDCl_3$) $\delta$ = 7.29-7.21 (10H, m, arom H), 4.03 (1H, d, $J$ = 10.2 Hz, $CH_2$), 3.76 (1H, , d, $J$ = 9.0 Hz, $CH_2$), 3.59 (1H, d, $J$ = 10.2 Hz, $CH_2$), 3.37 (1H, d, $J$ = 9.0 Hz, $CH_2$), 2.13 (3H, s, OAc), 1.85 (2H, q, $J$ = 4.5 Hz, $CH_2$), 0.79 (3H, t, $J$ = 4.5 Hz, Me); $^{13}$C NMR ($CDCl_3$) $\delta$ = 209.6, 175.5, 169.2 (C=O), 143.6, 142.8 (arom C), 128.2, 128.1, 127.8, 127.5, 126.5, 125.7 (arom CH), 82.9 (quart C), 72.7 ($CH_2$), 50.4 (C-3), 41.3, 32.9 ($CH_2$), 22.2, 8.0 (Me). FAB HRMS (acetone/NBA/NaI) calcd for $C_{22}H_{22}O_5Na$ 389.1365 (M+Na). Found 389.1398.

**3-(2-Acetoxy-2,2-diphenylethyl)-3-isopropyltetrahydrofuran-2,4-dione (8dc):** Yield (132 mg, 72%); $R_f$ = 0.44 (EtOAc/hexane 3:7 v/v); colorless microcrystals (from $CHCl_3$); mp 157 °C; IR ($CHCl_3$) $\nu$ 1799, 1753 (C=O); $^1$H NMR ($CDCl_3$) $\delta$ = 7.31-7.21 (10H, m, arom H), 3.95 (1H, d, $J$ = 10.5 Hz, $CH_2$), 3.86 (1H, d, $J$ = 8.7, $CH_2$), 3.44 (1H, d, $J$ = 10.5 Hz, $CH_2$), 3.42 (1H, d, $J$ = 8.7, $CH_2$), 2.15 (3H, s, $CH_3$), 2.11 (1H, m, CH), 1.00 (3H, d, $J$ = 4.2 Hz, Me), 0.98 (3H, d, $J$ = 4.2 Hz, Me); $^{13}$C NMR ($CDCl_3$) $\delta$ = 209.6, 175.3, 169.3 (C=O), 143.9, 142.7 (arom C), 128.2, 128.1, 127.8, 127.6, 126.8, 125.7 (arom CH), 82.9 (quart C), 72.7 ($CH_2$), 52.6 (C-3), 39.7 ($CH_2$), 22.3 (CH), 38.0, 17.4, 16.4 (Me). FAB HRMS (acetone/NBA/NaI) calcd for $C_{22}H_{21}O_5Na$ 403.1521 (M+Na). Found 403.1500.

**3-[2-Acetoxy-2,2-bis(4-chlorophenyl)ethyl]-3-benzyltetrahydrofuran-2,4-dione (8fa):** Yield (132 mg, 53%); $R_f$ = 0.56 (EtOAc/hexane 3:7 v/v); colorless microcrystals (from $CHCl_3$); mp 206-207 °C; IR (KBr) $\nu$ 1799, 1743 (C=O); $^1$H NMR ($CDCl_3$) $\delta$ = 7.19-6.89 (13H, m, arom H), 3.76 (1H, d, $J$ = 9.0 Hz, $CH_2$), 3.45 (1H, d, $J$ = 10.4 Hz, $CH_2$), 3.35 (1H, d, $J$ = 9.0 Hz, $CH_2$), 3.09 (1H, d, $J$ = 7.4 Hz, $CH_2$), 2.954 (1H, d, $J$ = 10.4 Hz, $CH_2$), 2.945 (1H, d $J$ = 7.4 Hz, $CH_2$), 2.06 (OAc). $^{13}$C NMR ($CDCl_3$) $\delta$ = 209.0, 174.9, 169.1 (C=O), 141.8, 141.0, 134.1, 133.8, 132.1 (arom C), 129.8, 128.7, 128.6, 128.4, 128.0, 127.9, 127.2 (arom CH), 82.1 (quart C), 72.8 ($CH_2$), 52.7 (C-3), 45.5, 41.3 ($CH_2$), 22.1 (OAc). FAB HRMS (acetone/NBA/NaI) calcd for $C_{27}H_{22}{}^{35}Cl_2O_5Na$ 519.0742 (M+Na). Found 519.0753.

**3-(2-Acetoxy-2,2-diphenylethyl)-3-pentyltetrahydrofuran-2,4-dione (8gc):** Yield (6 mg, 3%); $R_f$ = 0.73 (EtOAc/hexane 3:7 v/v); colorless needles (from $CHCl_3$); mp 96-97 °C; IR ($CHCl_3$) $\nu$ 1797, 1755

(C=O); $^1$H NMR ($CDCl_3$) $\delta$ = 7.29-7.21 (10H, m, arom H), 4.04 (1H, d, $J$ = 10.5 Hz, $CH_2$), 3.77 (1H, d, $J$ = 9.0 Hz, $CH_2$ ), 3.58 (1H, d, $J$ = 10.5 Hz, $CH_2$), 3.38 (1H, d, $J$ = 9.0 Hz, $CH_2$ ), 2.13 ( 3H, s, OAc), 1.80-1.77 (2H, m, $CH_2$), 1.25-1.12 (6H, m, $3CH_2$), 0.82 (3H, t, $J$ = 4.5 Hz, Me); $^{13}$C NMR ($CDCl_3$) $\delta$ = 209.7, 175.7, 169.2 (C=O), 143.6, 142.8 (arom C), 128.2, 127.8, 127.5, 126.6, 125.7 (arom CH), 83.0 (quart C), 72.7 ($CH_2$), 49.9 (C-3), 41.7, 39.7, 31.4, 23.0, 21.9 ($CH_2$), 22.2, 13.7 (Me). FAB HRMS (acetone/NBA/NaI) calcd for $C_{25}H_{28}O_5Na$ 431.1834 (M+Na). Found 431.1820.

**3-[2,2-Bis(4-chlorophenyl)ethenyl]-3-methyltetrahydrofuran-2,4-dione (9ba):** Yield (13.4 mg, 8%); $R_f$ = 0.72 (EtOAc/hexane 4:6 v/v); colorless microcrystals (from $CHCl_3$); mp 150-151 °C; IR (KBr) $\nu$ 1801, 1751 (C=O); $^1$H NMR ($CDCl_3$) $\delta$ = 7.34-6.93 (8H, m, arom H), 6.00 (1H, s, CH=), 4.31 (1H, d, $J$ = 10.2 Hz, $CH_2$), 3.38 (1H, d, $J$ = 10.2 Hz, $CH_2$), 1.53 (3H, s, Me); $^{13}$C NMR ($CDCl_3$) $\delta$ = 208.6, 176.1 (C=O), 137.8, 136.0, 134.9 (arom C), 131.5, 130.3, 129.1, 128.9, 128.8, 128.7, 128.5, 128.2 (arom CH), 145.3 ( quart C), 126.5 (CH), 72.2 ($CH_2$), 49.0 (C-3), 23.6 (Me). FAB HRMS (acetone/NBA/NaI) calcd for $C_{19}H_{14}Cl_2O_3Na$ 383.0218 (M+Na). Found 383.0210.

**3-Methyl-3-(2,2-diphenylethenyl)tetrahydrofuran-2,4-dione (9bc):** Yield (36.7 mg, 25%); $R_f$ = 0.50 (EtOAc/hexane 3:7 v/v); colorless liquid; IR ($CHCl_3$) $\nu$ 1805, 1757 (C=O); $^1$H NMR ($CDCl_3$) $\delta$ = 7.38-7.06 (10H, m, arom H), 6.08 (1H, s, CH=), 4.25 (1H, d, $J$ = 16.8 Hz, $CH_2$), 3.19 (1H, d, $J$ = 16.8 Hz, $CH_2$), 1.57 (3H, s, Me); $^{13}$C NMR ($CDCl_3$) $\delta$ = 209.1, 176.6 (C=O), 147.4, 139.8 (arom C), 128.7, 128.4, 128.3, 128.2, 126.9, 125.9 (arom CH), 138.2 ( quart C), 130.2 (CH), 72.1 ($CH_2$), 48.8 (C-3), 23.6 (Me). FAB HRMS (acetone/NBA/NaI) calcd for $C_{19}H_{16}O_3Na$ 315.0997 (M+Na). Found 315.1035.

**3-Ethyl-3-(2,2-diphenylethenyl)tetrahydrofuran-2,4-dione (9cc):** Yield (17.6 mg, 11%); $R_f$ = 0.59 (EtOAc/hexane 3:7 v/v); colorless liquid; IR ($CHCl_3$) $\nu$ 1803, 1755 (C=O); $^1$H NMR ($CDCl_3$) $\delta$ = 7.39-7.09 (10H, m, arom H), 6.09 (1H, s, CH=), 4.09 (1H, d, $J$ = 10.2 Hz, $CH_2$), 3.14 (1H, d, $J$ = 10.2 Hz, $CH_2$ ), 2.11 (2H, q, $J$ = 4.5 Hz, $CH_2$), 0.97 (3H, t, $J$ = 4.5 Hz, Me); $^{13}$C NMR ($CDCl_3$) $\delta$ = 209.6, 176.1 (C=O), 139.9, 138.4, (arom C), 130.3, 128.7, 128.4, 128.3, 128.2, 126.9 (arom CH), 147.3 (quart C), 125.6 (CH), 73.0 ($CH_2$), 53.9 (C-3), 31.9($CH_2$), 8.4 (Me). FAB HRMS (acetone/NBA/NaI) calcd for $C_{20}H_{18}O_3Na$ 329.1154 (M+Na). Found 329.1168.

**3-Isopropyl-3-(2,2-diphenylethenyl)tetrahydrofuran-2,4-dione (9dc):** Yield (30 mg, 18%); $R_f$ = 0.65 (EtOAc/hexane 3:7 v/v); colorless liquid; IR ($CHCl_3$) $\nu$ 1799, 1753 (C=O); $^1$H NMR ($CDCl_3$) $\delta$ = 7.38-7.09 (10H, m, arom H), 6.18 (1H, s, CH=), 4.02 (1H, d, $J$ = 9.9 Hz, $CH_2$), 3.13 (1H, d, $J$ =9.9 Hz, $CH_2$), 2.43-2.40 (1H, m, CH), 1.09 (3H, d, $J$ = 7.5 Hz, Me), 1.06 (3H, d, $J$ = 7.5 Hz, Me); $^{13}$C NMR ($CDCl_3$) $\delta$ = 209.1, 175.7 (C=O), 140.3, 138.4 (arom C), 130.4, 128.6, 128.3, 128.2, 128.1, 126.9 (arom CH), 147.1 quart C), 125.5 (CH), 73.2 ($CH_2$), 56.9 (C-3), 37.2 (CH), 17.5, 16.8 (Me). FAB HRMS (acetone/NBA/NaI) calcd for $C_{21}H_{20}O_3Na$ 321.1491 (M+Na). Found 321.1510.

**3-Butyl-3-(2,2-diphenylethenyl)tetrahydrofuran-2,4-dione (9ec):** Yield (232 mg, 70%); $R_f$ = 0.54 (EtOAc/hexane 3:7 v/v); colorless liquid; IR ($CHCl_3$) $\nu$ 1801, 1753 (C=O); $^1$H NMR ($CDCl_3$) $\delta$ = 7.39-7.09 (10H, m, arom H), 6.09 (1H, s, CH=), 4.09 (1H, d, $J$ = 10.5 Hz, $CH_2$), 3.13 (1H, d, $J$ = 10.5 Hz, $CH_2$), 2.06-2.03 (2H, m, $CH_2$), 1.33-1.17 (4H, m, $2CH_2$), 0.89 (3H, t, $J$ = 4.2 Hz, Me); $^{13}$C NMR ($CDCl_3$) $\delta$ = 209.6, 176.1 (C=O), 139.9, 138.4 (arom C), 130.3, 128.6, 128.4, 128.2, 126.9 (arom CH), 147.2 ( quart C), 125.9 (CH), 72.9 ($CH_2$), 53.5 (C-3), 38.6, 25.9, 22.6 ($CH_2$), 13.6 (Me). FAB HRMS (acetone/NBA/NaI) calcd for $C_{22}H_{22}O_3Na$ 357.1467 (M+Na). Found 357.1472.

**3-Benzyl-3-[2,2-bis(4-chlorophenyl)ethenyl]tetrahydrofuran-2,4-dione (9fa):** Yield (27.5 mg, 13%); $R_f$ = 0.59 (EtOAc /hexane 3:7 v/v); colorless microcrystals (from $CHCl_3$); mp 180-181 °C; IR (KBr) $\nu$ 1793, 1755 (C=O); $^1$H NMR ($CDCl_3$) $\delta$ = 7.28-6.92 (13H, m, arom H), 6.10 (1H, s, CH=), 3.40 (1H, d, $J$ = 7.8 Hz, $CH_2$), 3.28 (1H, d, $J$ =7.5 Hz, $CH_2$), 3.00 (2H, s, $CH_2$); $^{13}$C NMR ($CDCl_3$) $\delta$ = 209.5, 175.4 (C=O), 145.1, 138.0, 136.2, 134.9, 134.7, 132.4 (arom C), 131.5, 129.7, 129.1, 128.9, 128.6, 128.2, 128.2, (arom CH), 128.7 (quart C), 126.4 (CH), 73.2 ($CH_2$), 56.4 (C-3), 44.9 ($CH_2$). FAB HRMS (acetone/NBA/NaI) calcd for $C_{25}H_{18}Cl_2O_3Na$ 459.0531 (M+Na). Found 459.0566.

**3-Pentyl-3-(2,2-diphenylethenyl)tetrahydrofuran-2,4-dione (9gc):** Yield (61 mg, 35%); $R_f$ = 0.81 (EtOAc/hexane 3:7 v/v); colorless needles (from $CHCl_3$); mp 111-113 °C; IR ($CHCl_3$) $\nu$ 1799, 1755 (C=O); $^1$H NMR ($CDCl_3$) $\delta$ = 7.39-7.08 (10H, m, arom H), 6.09 (1H, s, CH=), 4.09 (1H, d, $J$ = 10.5 Hz, $CH_2$), 3.13 (1H, d, $J$ = 10.5 Hz, $CH_2$ ), 2.06-2.02 (2H, m, $CH_2$), 1.36-1.27 (6H, m, $3CH_2$), 0.87 (3H, t, $J$ = 4.2 Hz, Me); $^{13}$C NMR ($CDCl_3$) $\delta$ = 209.6, 176.1 (C=O), 147.1 (quart C), 139.9, 138.4 (arom C), 130.3, 128.6, 128.4, 128.2, 126.9 (arom CH), 125.9 (CH=), 72.9 ($CH_2$), 53.6 (C-3), 38.7, 31.6, 23.4, 22.1 ($CH_2$), 13.8 (Me). FAB HRMS (acetone/NBA/NaI) calcd for $C_{23}H_{24}O_3Na$ 371.1623 (M+Na). Found 371.1644.

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