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Mn(III)-BASED OXIDATIVE RADICAL RING-EXPANSION REACTION USING SQUARATE DERIVATIVES: SELECTIVE SYNTHESIS OF BIS(BUTENOLIDE)S AND THE ACETATE MONOMERS†

Jun-ichi Sasaki,[a] Makoto Kobayashi,[a] Yûsuke Ibe,[a] and Hiroshi Nishino[b]*

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

†This paper is dedicated to Professor Tohru Fukuyama on the occasion of his 70th birthday.

Abstract – The Mn(III)-based oxidation of phenyl- and alkyl-substituted hydroxycyclobutenones selectively produced the bis(butenolide)s or the acetate monomers via the 5-*endo* radical cyclization depending upon the concentration of the reaction. A similar reaction of hydroxycyclobutenones bearing an alkenyl and alkynyl substituent did not produce any bis(butenolide)s or acetate monomers, but the 5-*exo* and 6-*endo* radical cyclization products including the unsaturated group. The oxidation of the hydroxycyclobutenones having an unsaturated substituent in the presence of alkenes afforded radical coupling products during the 5-*exo* radical cyclization. The reaction details, structure determination of the products, and the mechanism for the formation of the products are described.

INTRODUCTION

3,4-Dihydroxycyclobut-3-ene-1,2-dione (squaric acid) and the dialkoxyl derivatives (dialkyl squarates) are multifunctional compounds including hydroxyl or alkoxyl and α,β-unsaturated carbonyl moieties, and consist of the characteristic strained cyclobutene framework, so that the squaric acid and the derivatives have been widely studied in the physical,[1] inorganic,[2] organic,[3] material,[4] and biological chemistry fields[5] for several decades. Especially, the strained structure is very attractive for bond-breaking and successive ring-expansion through re-bonding. For example, this strategy has been used for the synthesis of many

heterocyclic compounds and natural products such as a useful C-4 synthon.[6] Recently, we found that manganese(III) acetate, $Mn(OAc)_3•2H_2O$, effectively functioned in strong acidic media as an oxidative radical initiator.[7a] Since squaric acid is also a strong organic acid (pK_{a1} = 0.52; pK_{a2} = 3.48),[8] we were very interested in the use of squaric acid in the $Mn(OAc)_3$ oxidation system. We then studied the oxidation of squaric acid alone and in the presence of alkenes. Although the oxidant was quickly consumed in these reactions, no products were isolated and the starting materials were recovered. In order to break the strained cyclobutenedione scaffold, the 1,2-adduct, such as 4-hydroxy-4-phenylcyclobut-2-en-1-one,[9] was next examined in the Mn(III)-based reaction because it is known that the nucleophilic addition to the carbonyl group of squaric acid gave 4-hydroxycyclobutenones which were subject to various ring-transformation reactions.[10] Fortunately, the reaction proceeded, and new dimeric and monomeric products were isolated. Although the reactions with Pb(IV) and Pd(II) producing unique butenolide and 2-methylenecyclopentenedione derivatives are well-documented,[11] to the best of our knowledge, the oxidation using $Mn(OAc)_3$ has never been investigated. It is generally known that the oxy radicals were generated by the reaction of alcoholic and phenolic compounds with $Mn(OAc)_3$ during the oxidative decomposition of the alkoxy- and phenoxy-Mn(III) complex, and subsequently cyclized at the position of δ or ε from the hydroxyl group, finally producing five- or six-membered cyclic ethers.[12] For example, Kurosawa reported that the 2'-hydroxychalcons underwent oxidation to produce aurones in good yields.[13] Similar reactions of the 2'-hydroxybenzophenones, 2-hydroxystilbenes, and 2'-hydroxy-2-methylisoflavones afforded the corresponding xanthen-9-ones,[14] 2-arylbenzofurans,[15] and 5a-methyl-5a,10b-dihydro-11*H*-benzofuro[2,3-*b*]chromen-11-ones[16] containing five- or six-membered cyclic ethers. We then studied the Mn(III)-based reaction using various hydroxysquarate derivatives to anticipate the synthesis of new oxygen-heterocycles.

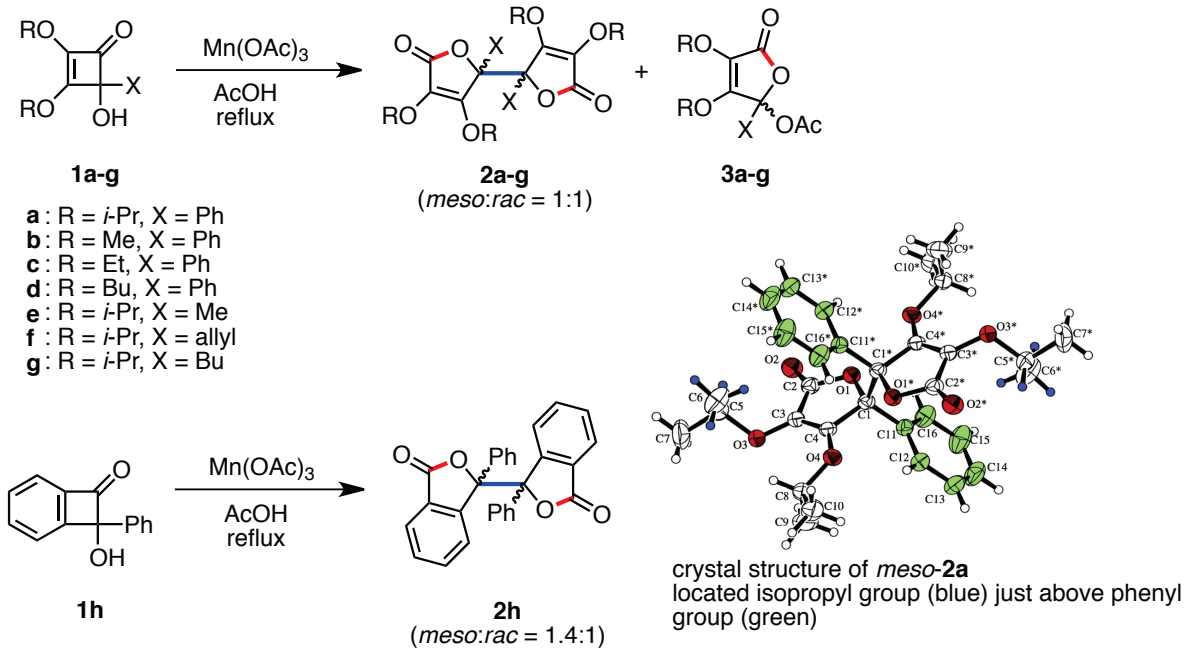
RESULTS AND DISCUSSION

Mn(III)-Based Oxidation of Hydroxycyclobutenones 1a-h

4-Substituted 2,3-dialkoxy-4-hydroxycyclobut-2-en-1-ones **1a-g** were synthesized by the nucleophilic addition of dialkyl squarates which were prepared by the heating of squaric acid in the corresponding alcohols (See Experimental section).[9] 2-Hydroxy-2-phenylbenzocyclobuten-1-one (**1h**) was prepared by the Grignard reaction of benzocyclobutene-1,2-dione (Also see Experimental section).[17,18] With the desired hydroxycyclobutenones **1a-h** in hand, we selected 4-hydroxy-2,3-diisopropoxy-4-phenylcyclobut-2-en-1-one (**1a**) as a typical squarate derivative, and investigated the oxidation using $Mn(OAc)_3$ (Scheme 1). When the reaction was carried out at the molar ratio of **1a**:$Mn(OAc)_3$ = 1:2 in boiling AcOH (25 mL), the reaction was finished in 1 h and two products were obtained; one was a 1:1 diastereoisomiric mixture of the dimeric product **2a** (FAB MS *m/z* 551 (M+H)) and the other was an

acetate monomer **3a** (Table 1, Entry 1). Since one of the dimeric stereoisomers was a crystalline solid, the fractional recrystallization was performed from CH_2Cl_2-hexane to give the *meso*-**2a**, and the residual solid obtained from the filtrate was recrystallized from MeOH, yielding *rac*-**2a**. The final filtrate was separated by silica gel column chromatography to afford the acetate **3a**. Both of the products **2a** and **3a** did not bear a hydroxyl group based on the IR spectrum, and the ring expansion involving the hydroxyl group of **1a** undoubtedly occurred from the fact that the signals of the carbonyl (δ *ca.* 168) and sp^2 carbons (δ *ca.* 158 and 120), except for the aromatic carbons, shifted upfield compared to those of **1a** (δ *ca.* 184, 166, and 133, respectively) in the ^{13}C NMR spectrum. Although the IR and ^{13}C NMR spectra of *meso*-**2a** and *rac*-**2a** were quite similar, the chemical shifts in the ^{1}H NMR spectra were characteristic, that is, one couple of methine (δ 4.35) and methyl protons (δ 0.57) of the isopropyl groups in *meso*-**2a** was shielded by the ring current effect of the phenyl groups. This meant that *meso*-**2a** should be a symmetrical structure. Gratifyingly, we obtained the X-ray single crystal structures of both dimeric products and determined the exact structures of *meso*-**2a** and *rac*-**2a** (See Experimental section). The spectroscopic data of the acetate monomer **3a** were also similar to those of the dimeric butenolide **2a** except for the existence of an acetoxyl group and quaternary carbon attached to two oxygens (δ *ca.* 99). Although the acetate **3a** gradually decomposed at room temperature, we could convert the acetate **3a** into the stable hemiacetal **3a'** which was characterized as 5-hydroxy-3,4-diisopropoxy-5-phenylfuran-2(5*H*)-one.

It was obvious that the dimeric butenolide **2a** was produced during the Mn(III)-based oxidative radical coupling reaction, therefore, not more than one equivalent of the oxidant is needed to only produce the corresponding alkoxyl radical, and the reaction under concentrated conditions might be superior to



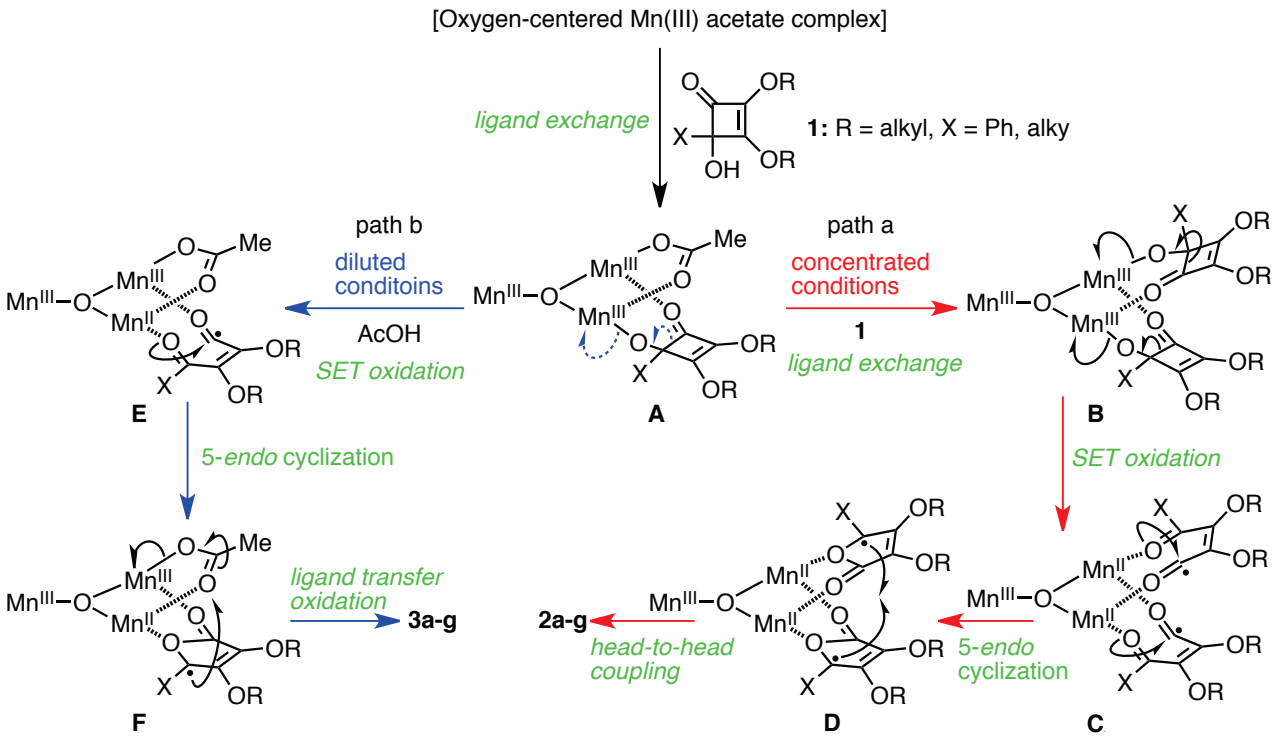
Scheme 1. Oxidation of Hydroxycyclobutenones **1a-h** with $Mn(OAc)_3$

Table 1. Oxidation of Hydroxycyclobutenones **1a-h** with $Mn(OAc)_3$[a]

Entry	Squarate **1**/	R	X	**1**:$Mn(OAc)_3$[b]	AcOH/mL	min	Product yield/%[c]	
1	**1a**	*i*-Pr	Ph	1:2	25	60	**2a** (68)	**3a** (15)
2	**1a**	*i*-Pr	Ph	1:1	5	60	**2a** (76)	**3a** (15)
3	**1a**	*i*-Pr	Ph	1:1	1	45	**2a** (83)	**3a** (10)
4	**1b**	Me	Ph	1:1	1	45	**2b** (80)	**3b** (16)
5	**1c**	Et	Ph	1:1	1	45	**2c** (75)	**3c** (11)
6	**1d**	Bu	Ph	1:1	1	45	**2d** (65)	**3d** (12)
7	**1e**	*i*-Pr	Me	1:1	1	1	**2e** (77)	–
8	**1f**	*i*-Pr	allyl	1:1	1	1	**2f** (77)	–
9	**1g**	*i*-Pr	Bu	1:1	1	1	**2g** (70)	**3g** (3)
10	**1h**	–	–	1:2	5	0.5	**2h** (80)	–
11	**1a**	*i*-Pr	Ph	1:4	250	30	**2a** (10)	**3a** (71)
12	**1b**	Me	Ph	1:4	250	30	**2b** (10)	**3b** (68)
13	**1c**	Et	Ph	1:4	250	30	**2c** (12)	**3c** (66)
14	**1d**	Bu	Ph	1:4	250	30	**2d** (13)	**3d** (62)
15	**1e**	*i*-Pr	Me	1:4	100	10	–	**3e** (70)
16	**1f**	*i*-Pr	allyl	1:3	100	2	–	**3f** (50)
17	**1g**	*i*-Pr	Bu	1:4	100	5	–	**3g** (84)
18	**1h**	–	–	1:4	100	5	**2h** (79)	–

[a] The reaction of squarate **1** (0.5 mmol) was carried out in boiling AcOH.
[b] Molar ratio. [c] Isolated yield.

accelerate the dimerization reaction. On the other hand, the acetate monomer **3a** should be an over-oxidation product, so that the use of an excess amount of the oxidant and the depression of the dimerization under diluted conditions might cause an increase in the yield. In order to control the reaction based on this hypothesis, we scrutinized the reaction. As a result, the dimerization could be controlled by using one equivalent of Mn(III) and 1 mL of the solvent, mainly giving **2a** (Entry 3), while the acetate monomer **3a** was mainly produced by using four equivalents of Mn(III) in 250 mL of AcOH (Entry 11). We then conducted the reaction of other dialkyl squatrates **1b-g** under the concentrated conditions, mainly producing the corresponding dimeric butenolides **2b-g** (Entries 4-9), while the reaction under the diluted conditions resulted in the selective production of the acetate monomers **3b-g** (Entries 12-17). Unfortunately, the meso and racemic bis(butenolide)s **2b-g** were simultaneously produced as a 1:1 diasteroisomeric mixture and the selectivity could not be controlled during the reaction. The reaction of the squarate analogue **1h** was also explored. However, the well-known bis(benzofuranone) **2h**[19] was only obtained as a 1.4:1 meso and racemic mixture under both conditions, and the acetate was not detected (Entries 10 and 18). The NMR spectrum of the dialkyl-substituted bis(butenolide)s **2e-g** deserves comments. The proton and carbon signals of both butenolide parts in the symmetrical *meso*-**2e-g** completely overlapped, however, those of the *rac*-**2e-g** showed a splitting pattern. Fortunately, a single crystal of *meso*-**2f** was successfully grown from Et_2O/hexane and analyzed by X-ray crystallography (See Experimental section).



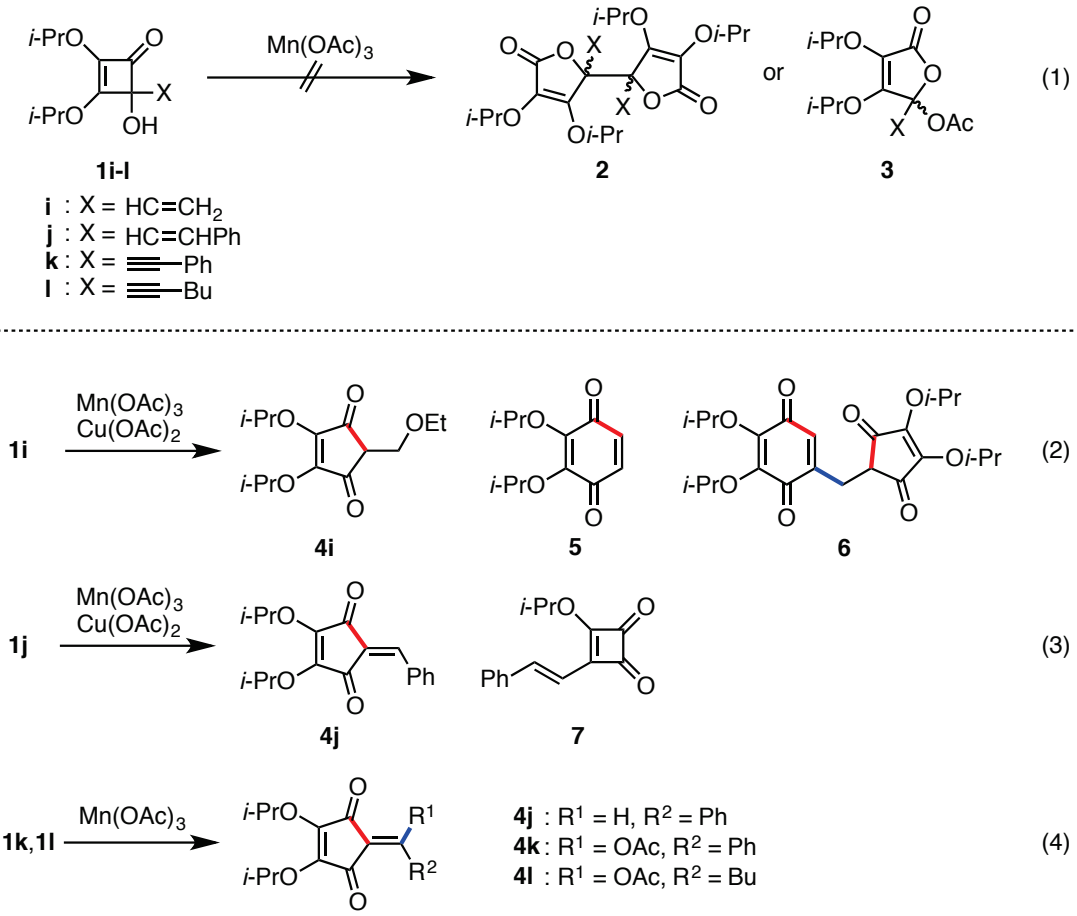
Scheme 2. Mechanism for the Formation of the Bis(butenolide) **2** and the Acetate **3**

The mechanism for the formation of bis(butenolide) **2** and the acetate monomer **3** could be explained as follows (Scheme 2); the alkoxy-Mn(III) complex **A** would be generated during the first stage by the acetate ligand-exchange reaction of $Mn(OAc)_3$ with the 4-hydroxycyclobutenones **1**. The oxygen-centered triangle structure of the Mn(III) complex should be essential for the generation of **A**.[20] When the reaction was carried out under concentrated conditions (path a), the dialkoxy-Mn(III) complex **B** would be inevitably formed by the reaction with another 4-hydroxycyclobutenone **1**. Once the complex **B** was generated, a single-electron transfer (SET) oxidation might automatically occur in each of the cyclobutenone ligands, producing acyl radicals **C** in the inner sphere of the complex to remove the ring strain. Since the acyl radicals **C** still coordinate in the inner sphere, 5-*endo* cyclization of the acyl radicals easily proceeds to generate the butenolide radicals such as **D**. Both butenolide radicals must be generated at the cross position because of the coordination, then head-to-head radical coupling should take place to finally form the bis(butenolide) **2**. The stereocontrol in the coupling reaction would be impossible during the stages **B**, **C**, and **D**, so that meso and racemic bis(butenolide)s **2** must be produced as a 1:1 diastereoisomeric mixture. On the other hand, when the reaction was conducted under diluted conditions (path b), the SET oxidation should occur at the early stage of the alkoxy-Mn(III) complex **A** because of the high dilution conditions and the existence of the abundant $Mn(OAc)_3$, producing the acyl radical **E**. The acyl radical **E** generated in the coordination sphere would take the place of the 5-*endo* cyclization similar to the acyl radicals **C**, producing the butenolide radical **F**. Since radical **F** still coordinates to the acetate complex, the acetate-ligand transfer oxidation at stage **F** probably takes place, finally affording

the acetate monomer **3**. It was considered that the formation of the alkoxy-Mn(III) complex **A** must be the rate-determining step of the reaction, because it took a long reaction time when the 4-hydroxycyclobutenones **1** having a large substituent X, such as a phenyl group, were used (Entries 1-6 and 11-14), while the oxidation of **1** bearing a rather smaller X, such as the alkyl group, was completed in a relatively shorter reaction time (Entries 7-9 and 15-17). The mechanism is briefly depicted in Scheme 2. The reason why the bis(benzofuranone) **2h** was predominantly produced regardless of the reaction concentration might be that the bis(benzocyclobutenone) complex corresponding to complex **B** would be easy to form because of the π–π stacking interaction between both benzocyclobutenone ligands.

Oxidation of Hydroxycyclobutenones 1i-l Having an Alkenyl and Alkynyl Substituent

Since we were pleased to develop the ring-expansion of the hydroxycyclobutenones **1a-h** during the 5-*endo* cyclization of the acyl radicals, we were next interested in the reaction of the hydroxycyclobutenones bearing an alkenyl and alkynyl group. The alkenyl and alkynyl-substituted 4-hydroxy-2,3-diisopropylcyclobutenones **1i-l** were then prepared according to the method mentioned above, and a similar reaction of **1i-l** was carried out under various conditions. As a result, it gave a complex mixture, and no bis(butenolide)s **2** and acetate monomers **3** were isolated (Scheme 3, eq. (1) and Table 2, Entries 1, 2). It was speculated that the 5-*endo* cyclization of acyl radicals, such as **C** and **E**, in Scheme 2 did not occur at the acyl oxygen, but the alkenyl and alkynyl substituents, that is, 5-*exo*- and/or 6-*endo*-mode cyclization would preferentially take place, affording primary and/or secondary radicals.[3b,10a,11a,e,18] It was reported that the primary and secondary radicals could not be oxidized by Mn(III),[20f,21] therefore, the reaction must be complicated because of the radical chain reaction. In order to control the oxidative radical reaction, the reaction was carried out in the presence of $Cu(OAc)_2$ as a co-oxidant according to Snider's method.[21] As a result, the reaction of vinylcyclobutenone **1i** afforded the 6-*endo* cyclization products **5** and **6** together with a small amount of the 5-*exo* product **4i** (eq. (2) and Entries 3-5, also see Scheme 4). Styrylcyclobutenone **1j** also underwent the reaction to produce the 5-*exo* product **4j** (eq. (3) and Entries 6-9). Interestingly, the rearrangement product **7** was also obtained in the reaction in AcOH (Entry 10). Although the strong acid-catalyzed rearrangement of **1j** was known,[9,22] the rearrangement product **7** was easily produced in boiling AcOH (Entry 11) (See Experimental section). The oxidation of phenylethynyl- **1k** and 1-hexyn-1-yl-cyclobutenone **1l** with $Mn(OAc)_3$ resulted in the 5-*exo* products **4j-l** (eq. (4) and Entries 12, 13, 15). The reaction of **1k** with $Mn(pic)_3$ instead of $Mn(OAc)_3$ also gave **4j** in a moderate yield (Entry 14). Although the reactions of the alkenyl and alkynyl-substituted 4-hydroxy-2,3-diisopropylcyclobutenones **1i-k** were conducted under various conditions, in any event, it was difficult to control the reaction and improve the product yield.



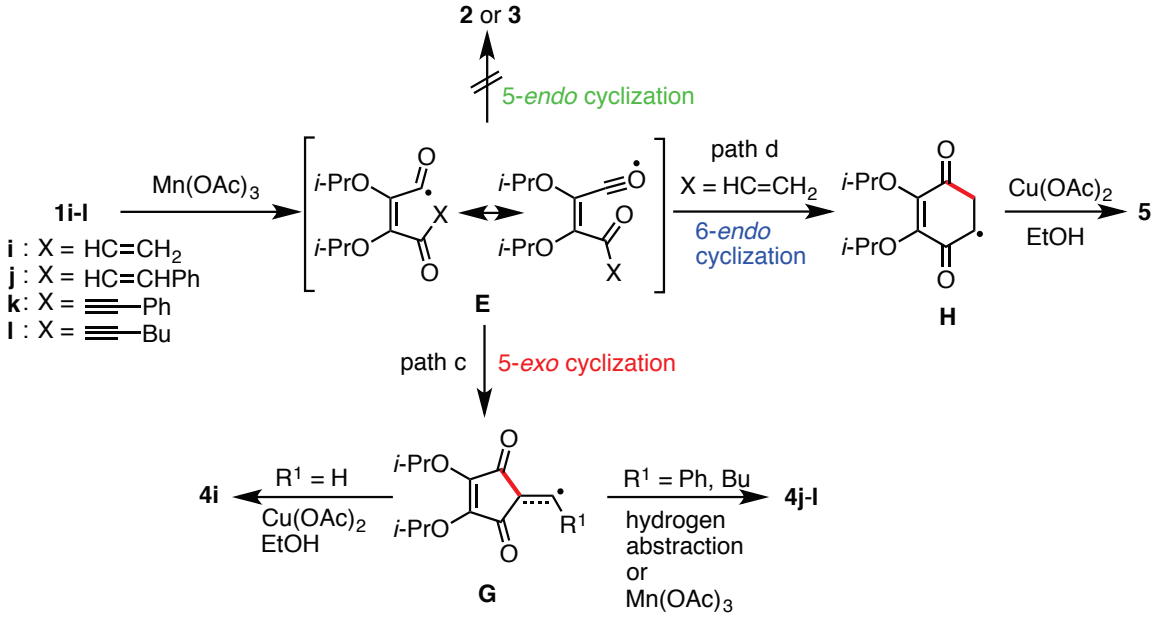
Scheme 3. Oxidation of Hydroxycyclobutenones **1i-l** Bearing an Alkenyl and Alkynyl Substituent

Table 2. Oxidation of Hydroxycyclobutenones **1i-l** Bearing an Alkenyl and Alkynyl Substituent[a]

Entry	Squarate **1**/	X	**1**:$Mn(OAc)_3$[b]	Solvent/mL	Tempertature	Time	Product yield/%[c]		
1	**1i**	vinyl	1:1	AcOH/1	reflux	0.5 min	c.m.[d]		
2	**1i**	vinyl	1:1	AcOH/25	reflux	2 min	c.m.[d]		
3	**1i**	vinyl	1:2:1[e]	EtOH/10	rt	21 h	**4i** (4)	**5** (31)	**6** (trace)
4	**1i**	vinyl	1:1:1[e]	EtOH/10	reflux	5 min	–	**5** (26)	–
5	**1i**	vinyl	1:2:1[e]	EtOH/10	reflux	5 min	–	**5** (27)	**6** (9)
6	**1j**	styryl	1:2	EtOH/10	rt	48 h	**4j** (13)		
7	**1j**	styryl	1:2	EtOH/10	reflux	5 min	**4j** (12)		
8	**1j**	styryl	1:1:1[e]	EtOH/10	rt	2.5 h	**4j** (30)		
9	**1j**	styryl	1:1.5:1[e]	EtOH/10	reflux	5 min	**4j** (36)		
10	**1j**	styryl	1:1.5:1[e]	AcOH/10	reflux	3 min	**4j** (38)	**7** (34)	
11	**1j**	styryl	–	AcOH/10	reflux	30 min		**7** (quant)	
12	**1k**	phenylethynyl	1:2	AcOH/10	rt	6 h	**4j** (31)	**4k** (20)	
13	**1k**	phenylethynyl	1:2	AcOH/100	reflux	3 min	**4j** (22)	**4k** (trace)	
14	**1k**	phenylethynyl	1:2[f]	DMF/10	80 °C	1.5 h	**4j** (40)		
15	**1l**	1-hexyn-1-yl	1:2	AcOH/10	rt	24 h	**4l** (51)		

[a] The reaction of squarate **1** (0.5 mmol) was carried out in a solvent under argon.
[b] Molar ratio. [c] Isolated yield. [d] Complex mixture. [e] Molar ratio of **1**:$Mn(OAc)_3$:$Cu(OAc)_2$. [f] $Mn(pic)_3$ was used instead of $Mn(OAc)_3$.

The mechanism could be understood such that acyl radicals **E** should be generated via the alkoxy-Mn(III) complex as **A** in Scheme 2, and the 5-*exo* (path c) and 6-*endo*-mode cyclization (path d) predominantly occur because of the high reactivity of the alkenyl and alkynyl groups, producing the 5-*exo* **4** and 6-*endo* cyclization products **5** (Scheme 4). These results were in contrast to those of the oxidation using $Pb(OAc)_4$.[11a] The $Cu(OAc)_2$ as a co-oxidant was indispensable for the termination of the Mn(III)-based radical reaction, otherwise, the radical chain reaction could not be controlled. A small amount of ((dioxocyclopentenyl)methyl)-1,4-benzoquinone **6** would probably be formed by the oxidative coupling reaction of the radical intermediates **G** and **H**.

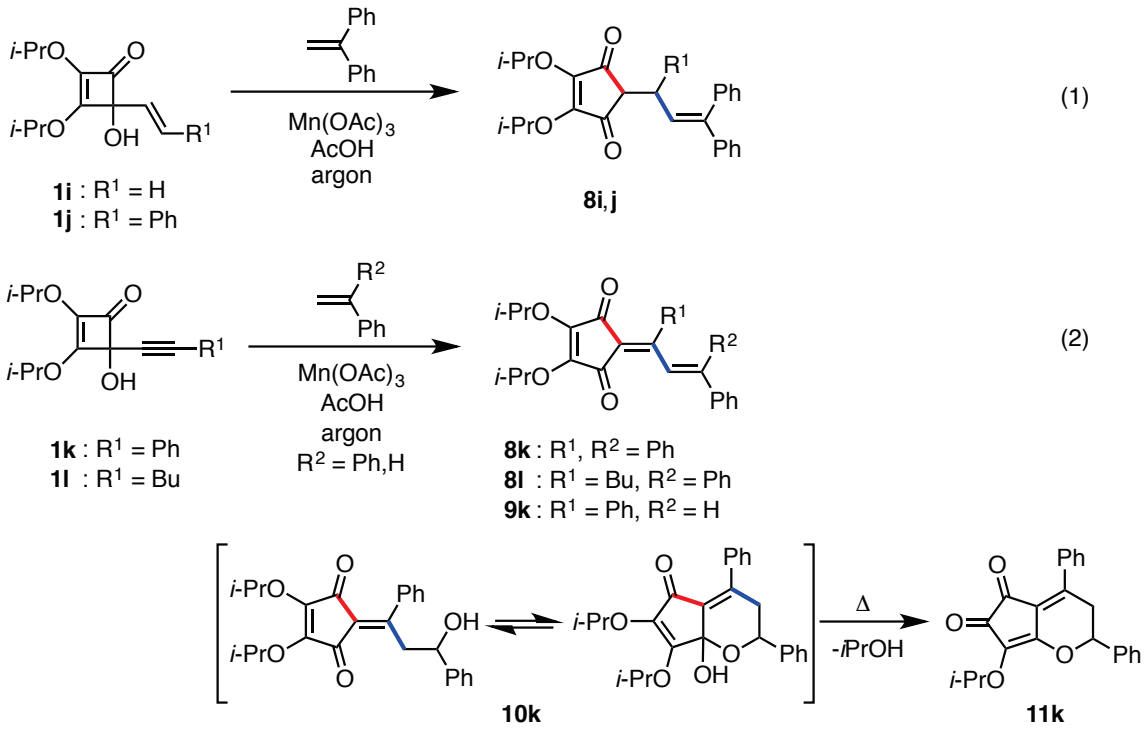


Scheme 4. Reaction Pathway in the Oxidation of Hydroxycyclobutenones **1i-l**

Mn(III)-Based Reaction of Hydroxycyclobutenones 1i-l with Alkenes

With the 5-*exo* and 6-*endo* radical cyclization including unsaturated bonds in hand, we next expected to produce bicyclic heterocycles and attempted to trap the radical intermediates **G** and **H** with an alkene scavenger. First of all, we undertook the reaction of vinylcyclobutenone **1i** in the presence of 1,1-diphenylethene (Scheme 5). In spite of the complicated reaction, a coupling product, such as **8i**, was barely obtained under various conditions (eq. (1) and Table 3, Entries 1-4). However, no similar coupling product, such as **8j**, was detected in the reaction of styrylcyclobutenone **1j** except for the homocyclization product **4j** and rearrangement product **7** (Entry 5). It was difficult to deduce the structure of **8i** because two carbonyl carbons (δ 194), two sp^2 carbons (δ 151) in the cyclopentenedione, and two methines (δ 75) and two sets of methyl carbons (δ 22.94 and 22.92) in the isopropoxyl group overlapped in the ^{13}C NMR spectrum due to the symmetrical structure. Finally, the structure of **8i** was determined by an X-ray crystallographic analysis (See Experimental section). The reaction of phenylethynylcyclobutenone **1k**

efficiently proceeded and resulted in the coupling product **8k** in 75% yield (eq. (2) and Entry 7). However, a similar reaction of 1-hexyn-1-ylcyclobutenone **1l** afforded the coupling product **8l** in a somewhat low yield (eq. (2) and Entry 9).



Scheme 5. Mn(III)-based Reaction of Squarates **1i-l** with Alkenes

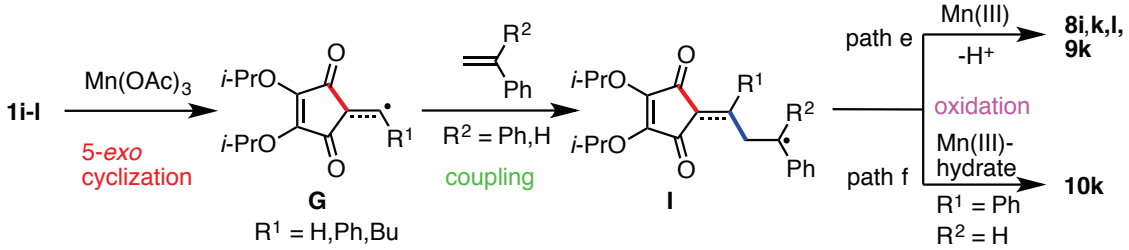
Table 3. Mn(III)-based Reaction of Squarates **1i-l** with Alkenes[a]

Entry	Squarate **1**/	R^1	Alkene	**1**:$Mn(OAc)_3$[b]	Solvent/mL	Tempertature	Time	Product yield/%[c]	
1	**1i**	H	1,1-diphenylethene	1:2	AcOH/10	80 °C	2 min	**8i** (10)	
2	**1i**	H	1,1-diphenylethene	1:2	AcOH/10	reflux	2 min	**8i** (22)	
3	**1i**	H	1,1-diphenylethene	1:4	AcOH/10	reflux	2 min	**8i** (20)	
4	**1i**	H	1,1-diphenylethene	1:2	AcOH/50	reflux	2 min	**8i** (13)	
5	**1j**	Ph	1,1-diphenylethene	1:2	AcOH/10	rt	5 d	**8j** (nd)[d]	
6	**1k**	Ph	1,1-diphenylethene	1:2	AcOH/25	rt	4 h	**8k** (31)	
7	**1k**	Ph	1,1-diphenylethene	1:2	AcOH/25	80 °C	5 min	**8k** (75)	
8	**1k**	Ph	1,1-diphenylethene	1:2	AcOH/25	reflux	2 min	**8k** (59)	
9	**1l**	Bu	1,1-diphenylethene	1:2	AcOH/10	rt	19 h	**8l** (20)[e]	
10	**1k**	Ph	styrene[f]	1:1.8	AcOH/100	rt	1.5 h	**9k** (10)[g]	**10k** (34)
11	**1k**	Ph	styrene	1:2	AcOH/10	80 °C	5 min	**9k** (9)[g]	**10k** (22)
12	**1k**	Ph	styrene	1:2	EtOH/10	reflux	3 min	**9k** (nd)[h]	**10k** (17)
13	**1l**	Bu	styrene	1:2	AcOH/10	rt	24 h	n.d.[i]	

[a] The reaction of squarate **1** (0.5 mmol) with an alkene (0.5 mmol) was carried out in AcOH under argon. [b] Molar ratio. [c] Isolated yield. [d] The couling product **8j** was not detected, but the homocyclization product **4j** (8%) and rearrangement product **7** (19%) were isolated. [e] The homocyclization acetate **4l** (8%) was also obtained. [f] Styrene (1.5 mmol) was used. [g] Homocyclization product **4j** (5-11%) was also produced. [h] The coupling product **9k** was not detected, but the homocyclization product **4j** (16%) and the acetate **4k** (18%) were isolated. [i] The coupling products were not detected, but the homocyclization acetate **4l** was isolated (see Table 2, Entry 15).

The use of styrene instead of 1,1-diphenylethene led a more complicated reaction due to the polymerization of styrene. Although the reaction of vinyl- **1i**, styryl- **1j**, and 1-hexyn-1-yl-cyclobutenones **1l** did not give any coupling products, an intractable mixture probably containing an equilibrium mixture of the alcohol **10k** was obtained from the reaction of phenylethynylcyclobutenone **1k** along with the coupling product **9k** (eq. (2) and Entries 9-12). The alcohol **10k** could be transformed into the stable diketone derivative **11k** (60% yield) by heating in acetone/H_2O (Scheme 5). The spectroscopic data of **11k** were in good agreement with those of 7-isopropoxy-2,4-diphenyl-2,3-dihydrocyclopenta[*b*]pyran-5,6-dione.

The reaction pathway is outlined in Scheme 6. The 5-*exo* cyclization product radicals **G** generated by path c described in Scheme 4 were certainly trapped by adding alkenes followed by oxidation to produce the coupling products **8**, **9**, and **10** via intermediate radicals **I** (Scheme 6). When 1,1-diphenylethene was used in the reaction, the intermediate radicals **I** (R^2 = Ph) tended to be oxidized and followed by deprotonation through the corresponding tertiary carbocation (path e). On the other hand, the use of styrene might allow the ligand-transfer oxidation by Mn(III)-hydrate on the intermediate radicals **I** (R^2 = H) to afford **10k** (path f). In any event, the use of the hydroxycyclobutenones **1i-l** bearing an alkenyl and alkynyl substituent was not practical for the synthesis of bicyclic compounds such as **11k** from the point of product yield.



Scheme 6. Proposed Mechanism for the Ring-Expansion Followed by Radical Trapping Reaction

CONCLUSION

We have accomplished the selective synthesis of bis(butenolide)s **2** and the acetate monomers **3** using phenyl- and alkyl-substituted hydroxycyclobutenones **1a-h** during the ring-expansion followed by the 5-*endo* radical cyclization reaction specialized by the oxygen-centered triangle Mn(III) complex. While the reaction using hydroxycyclobutenones **1i-l** having an alkenyl and alkynyl substituent did not allow the 5-*endo* cyclization to form the corresponding bis(butenolide)s **2** and the acetate monomers **3**, but the 5-*exo* and 6-*endo* radical cyclization including the unsaturated group to afford cyclopentenediones **4i-l** and benzoquinones **5**, **6** similar to the reaction using Pb(IV) and Pd(II).[10,11] We also revealed that the exomethylene-cyclopentenedione radicals, such as intermediate **G**, could be trapped by alkenes as a radical scavenger, producing coupling products **8j**,**k**,**l** and **9k** together with the bicyclic compound **10k**.[10]

In all cases, it was difficult to control the stereoselectivity of the bis(butenolide)s **2** and improve the product yield of the 5-*exo* **4** and 6-*endo* cyclization products **5** in addition to the coupling products **8** and **9** except for **8k**. Furthermore, a fundamental problem of the progress of this study is that 3,4-dihydroxycyclobut-3-ene-1,2-dione (squaric acid) as a starting material is quite expensive even if it is an attractive material and commercially available. Incidentally, it was known that the isomeric 4,4'-dimethyl-2,2'-diphenyl-[2,2'-bifuran]-5,5'(2*H*,2'*H*)-dione (25%) and 4-methyl-5-oxo-2-phenyl-2,5-dihydrofuran-2-yl acetate (7%) were obtained by the Mn(III)-based reaction of phenylacetylene with methylmalonic acid.[23]

EXPERIMENTAL

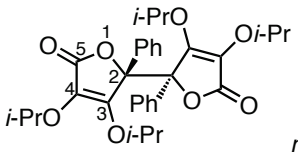
Measurements. Melting points were taken using a MP-J3 Yanagimoto micromelting point apparatus and are uncorrected. The IR spectra were measured in $CHCl_3$ or KBr using a Shimadzu 8400 FT IR spectrometer and expressed in cm^{-1}. The NMR spectra were recorded using a JNM ECX 500 or AL300 FT-NMR spectrometer at 500 MHz for the ^1H and at 125 MHz for ^{13}C, with tetramethylsilane as the internal standard. The chemical shifts are reported as δ values (ppm) and the coupling constants in Hz. The following abbreviations are used for the multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; and brs, broad singlet for the ^1H NMR spectra. The EI MS spectra were obtained by a Shimadzu QP-5050A gas chromatograph-mass spectrometer at the ionizing voltage of 70 eV. The high-resolution mass spectra using a JEOL JMS-700 MStation and the elemental analyses using a J-SCIENCE LAB JM10 were performed at the Instrumental Analysis Center, Kumamoto University, Kumamoto, Japan. The X-ray analysis was performed by a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo-Kα radiation, and the structure was solved by direct methods and expanded using Fourier techniques.

Materials. Manganese(II) acetate tetrahydrate, $Mn(OAc)_2 \cdot 4H_2O$, was purchased from Wako Pure Chemical Ind., Ltd. 3,4-Dihydroxycyclobut-3-ene-1,2-dione (squaric acid), 3,4-dibutoxycyclobut-3-ene-1,2-dione (dibutyl squarate), allyl bromide, styrene, β-bromostyrene, and 1-hexyne were purchased from Tokyo Kasei Co., Ltd. Vinylmagnesium bromide in tetrahydrofuran (THF), methyllithium in Et_2O, *n*-butyllithium in *n*-hexane, and *tert*-butyllithium in *n*-pentane were purchased from Kanto Chemical Co., Inc., and all commercially available materials were used as received. Flash column chromatography was performed on silica gel 60N (40-50 mm), which was purchased from Kanto Chemical Co., Inc., and preparative thin layer chromatography (TLC) on Wakogel B-10 and B-5F from Wako Pure Chemical Ind., Ltd. The solvents were commercially-available first-grade and used as received. 3,4-Diisopropoxycyclobut-3-ene-1,2-dione (diisopropyl squarate) was prepared by the heating of squaric acid (1.14 g, 10 mmol) in 2-propanol and benzene (1:1 v/v) for 5 days using a Dean-Stark

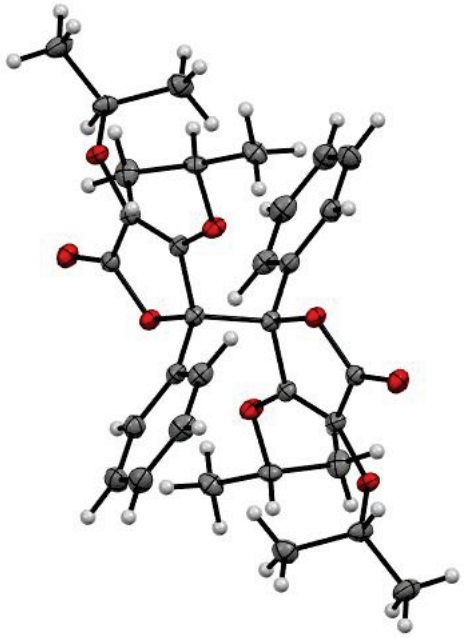
apparatus (1.82 g, 92% yield), mp 43 °C (lit,[9] mp 43-44 °C). Diisopropyl squarate was heated under reflux in absolute MeOH or EtOH for 3 days to give dimethyl squarate in 75% yield, mp 55 °C (lit,[24] mp 55 °C) or diethyl squarate in 82% yield, as a colorless liquid.[11,22] The 2,3-dialkoxy-4-hydroxy-4-phenylcyclobut-2-en-1-ones **1a-d** were synthesized by the reaction of the corresponding dialkoxyl squarate with phenyllithium prepared in situ by the reaction of bromobenzene with *n*-butyllithium in dry THF at -78 °C under argon, which gave **1a** in 90% yield as a yellowish oil;[9a] **1b** in 65% yield as a yellowish oil;[11a] **1c** in 78% yield, mp 95-98 °C (lit,[22] mp 96-98 °C); and **1d** in 70% yield. 4-Hydroxy-2,3-diisopropoxy-4-methylcyclobut-2-en-1-one (**1e**) and 4-butyl-4-hydroxy-2,3-diisopropoxycyclobut-2-en-1-one (**1g**) were prepared by the reaction of the corresponding alkyllithium in dry Et_2O at -78 °C under argon, which gave **1e** in 72% yield as colorless microcrystals, mp 35-36 °C and **1g** in 83% yield as a yellow oil.[9a] 4-Allyl-4-hydroxy-2,3-diisopropoxycyclobut-2-en-1-one (**1f**) and 4-hydroxy-2,3-diisopropoxy-4-vinylcyclobut-2-en-1-one (**1i**) were prepared by the Grignard reaction of diisopropyl squarate with allylmagnesium bromide and vinylmagnesium bromide in dry THF at -78 °C, affording **1f** in 54% yield as a yellowish solid, mp 37-38 °C and **1i** in 60% yield as a yellow oil.[25] (*E*)-4-Hydroxy-2,3-diisopropoxy-4-styrylcyclobut-2-en-1-one (**1j**) was obtained by the reaction of diisopropyl squarate with styryllithium prepared in situ by *β*-bromostyrene with *tert*-butyllithium in dry Et_2O at -78 °C in 78% yield as a yellowish solid, mp 83-85 °C. 4-Hydroxy-2,3-diisopropoxy-4-(phenylethynyl)cyclobut-2-en-1-one (**1k**) was synthesized by the reaction of diisopropyl squarate with phenylethynyllithium prepared in situ by *β*-bromostyrene with *n*-butyllithium in dry THF at -78 °C in 76% yield as a yellowish solid recrystallized from Et_2O/hexane, mp 104-105 °C (lit,[9a] mp 73-74 °C from CH_2Cl_2/hexane). 4-(Hex-1-yn-1-yl)-4-hydroxy-2,3-diisopropoxycyclobut-2-en-1-one (**1l**) was obtained by a similar reaction of the diisopropyl squarate with a mixture of 1-hexyne and *n*-butyllithium in 98% yield as a yellow oil.[9a] 2-Hydroxy-2-phenylbenzocyclobuten-1-one (**1h**)[17] was synthesized by the addition of benzyne from anthranic acid with 1,2-dichloroehtene to afford 1,1-dichlorobenzocyclobutane (68% yield) followed by hydrolysis to give benzocyclobutanone (72% yield), which was oxidized to give benzocyclobutanedione (60% yield) finally followed by the Grignard reaction with phenylmagnesium bromide (**1h**: 10% yield, as colorless microcrystals recrystallized from $CHCl_3$/hexane, mp 102-103 °C).[18] 1,1-Diphenylethene was prepared by the Grignard reaction of acetophenone with phenylmagnesium bromide followed by dehydration in 20% aqueous sulfuric acid.[26] Manganese(III) acetate dihydrate, $Mn(OAc)_3$•$2H_2O$, was synthesized according to our modified method.[27] Manganese(III) picolinate, $Mn(pic)_3$, was prepared by the reaction of $Mn(OAc)_3$•$2H_2O$ (6.03 g) with picolinic acid (8.31 g) in acetonitrile (200 mL) at 70 °C for 2 h (9.04 g; 94% yield).[28]

Reaction of 2,3-Dialkoxy-4-hydroxycyclobut-2-en-1-ones 1a-h under Highly Concentrated Conditions. To 2,3-dialkoxy-4-hydroxycyclobut-2-en-1-one **1** (0.5 mmol) in AcOH (1 mL),

$Mn(OAc)_3$•$2H_2O$ (0.5 mmol) was added. The mixture was heated under reflux until the Mn(III) oxidant was completely consumed and the brown color of Mn(III) turned transparent. The existence of the Mn(III) was monitored by iodine-starch paper and each reaction time is listed in Table 1. After completion of the reaction, water (10 mL) was added and the aqueous mixture was extracted with $CHCl_3$ (10 mL × 5). The combined extracts were washed with water (10 mL), a saturated aqueous solution of $NaHCO_3$ (10 mL), brine (10 mL), dried over anhydrous magnesium sulfate (3 g), then concentrated to dryness. The crude solid obtained from the reaction of **1a-d**,**h** was recrystallized from CH_2Cl_2/hexane, giving *meso*-**2a-d**,**h** and the residual solid from the filtrate was recrystallized from MeOH, yielding *rac*-**2a-d**. The residue obtained from the reaction of **2e-g** was separated by column chromatography on silica gel eluting with $CHCl_3$, mainly giving the corresponding bis(2-buten-4-olide) **2e-g** (Table 1).



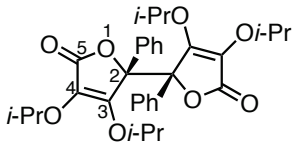
meso-**2a**



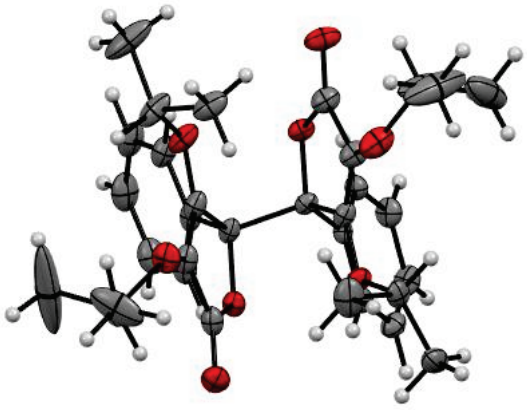
Crystal structure of *meso*-**2a**

***meso*-3,3',4,4'-Tetraisopropoxy-2,2'-diphenyl-[2,2'-bifuran]-5,5'(2*H*,2'*H*)-dione (*meso*-2a):** colorless needles (from CH_2Cl_2-hexane); mp 195-197 °C; IR ($CHCl_3$) ν 1759 (C=O), 1665 (C=C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90-7.85 (4H, m, arom H), 7.37-7.31 (6H, m, arom H), 5.07 (2H, sept, J = 6.3 Hz, >C<u>H</u>–O ×2), 4.35 (2H, sept, J = 6.3 Hz, >C<u>H</u>–O ×2), 1.42 (6H, d, J = 6.3 Hz, CH_3 ×2), 1.23 (6H, d, J = 6.3 Hz, CH_3 ×2), 1.02 (6H, d, J = 6.3 Hz, CH_3 ×2), 0.57 (6H, d, J = 6.3 Hz, CH_3 ×2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.3 (<u>C</u>=O ×2), 159.1 (2C) (C-3, C-3'), 134.5 (2C) (arom C), 129.2 (2C), 128.4 (4C), 127.1 (4C) (arom CH), 120.4 (2C) (C-4, C-4'), 83.1 (2C) (C-2, C-2'), 76.4 (2C), 73.2 (2C) (><u>C</u>H–O), 23.0 (2C), 22.6 (2C), 22.5 (2C), 21.3 (2C) (CH_3); FAB MS (MeOH/NBA) *m/z* (rel intensity) 551 (M+H, 15), 275 (97), 233 (100), 191 (95); FAB MS (MeOH/NBA/NaI) *m/z* (rel intensity) 573 (M+Na, 100), 275 (42), 233 (61), 191 (75). Anal. Calcd for $C_{32}H_{38}O_8$: C, 69.80; H, 6.96. Found: C, 69.65; H, 6.88. X-Ray crystallographic data: space group *P*bca (#61), orthorhombic, a = 16.9476(4), b = 16.2796(3), c = 10.6982(2) Å, V =

2954.6(2) Å^3, Z = 4, R = 0.034, R_w = 0.051, GOF = 1.09. X-Ray coordinates were deposited with the Cambridge Crystallographic Data Centre: *meso*-**2a**: CCDC 1866855.

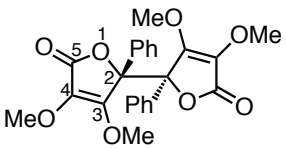


rac-**2a**



Crystal structure of *rac*-**2a**

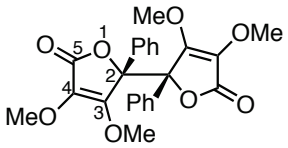
***rac*-3,3',4,4'-Tetraisopropoxy-2,2'-diphenyl-[2,2'-bifuran]-5,5'(2*H*,2'*H*)-dione (*rac*-2a):** colorless cubes (from MeOH); mp 156.0-157.5 °C; IR ($CHCl_3$) ν 1761 (C=O), 1669 (C=C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48-7.44 (4H, m, arom H), 7.23-7.10 (6H, m, arom H), 5.23 (2H, sept, J = 6.1 Hz, >C<u>H</u>–O ×2), 4.87 (2H, sept, J = 6.1 Hz, >C<u>H</u>–O ×2), 1.43 (6H, d, J = 6.1 Hz, CH_3 ×2), 1.30 (6H, d, J = 6.1 Hz, CH_3 ×2), 1.28 (6H, d, J = 6.1 Hz, CH_3 ×2), 1.13 (6H, d, J = 6.1 Hz, CH_3 ×2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.1 (<u>C</u>=O ×2), 158.6 (2C) (C-3, C-3'), 134.8 (2C) (arom C), 128.6 (2C), 127.42 (4C), 127.35 (4C) (arom CH), 119.8 (2C) (C-4, C-4'), 83.3 (2C) (C-2, C-2'), 75.5 (2C), 73.1 (2C) (>C<u>H</u>–O), 22.9 (2C), 22.6 (2C), 22.5 (2C), 22.3 (2C) (CH_3); FAB MS (MeOH/NBA) *m/z* (rel intensity) 551 (M+H, 6), 275 (91), 233 (97), 191 (100); FAB MS (MeOH/NBA/NaI) *m/z* (rel intensity) 573 (M+Na, 40), 275 (78), 233 (100), 191 (89). FAB HRMS (MeOH/NBA): calcd for $C_{32}H_{39}O_8$ 551.2645 (M+H); Found 551.2696. X-Ray crystallographic data: space group P1 (#2), triclinic, a = 15.2166(4), b = 16.7250(6), c = 13.6556(4) Å, α = 106.985(1)°, β = 92.543(1)°, γ = 62.963(1)°, V = 2944.5(2) Å^3, Z = 4, R = 0.060, R_w = 0.188, GOF = 1.05. X-Ray coordinates were deposited with the Cambridge Crystallographic Data Centre: *rac*-**2a**: CCDC 1866645.



meso-**2b**

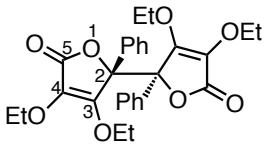
***meso*-3,3',4,4'-Tetramethoxy-2,2'-diphenyl-[2,2'-bifuran]-5,5'(2*H*,2'*H*)-dione (*meso*-2b):** colorless needles (from CH_2Cl_2-hexane); mp 278.5-279.0 °C; IR ($CHCl_3$) ν 1765 (C=O), 1675 (C=C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87-7.81 (4H, m, arom H), 7.41-7.38 (6H, m, arom H), 4.09 (6H, s, C<u>H</u>$_3$–O ×2), 3.26 (6H, s, C<u>H</u>$_3$–O ×2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.4 (<u>C</u>=O ×2), 160.2 (2C) (C-3, C-3'), 133.5 (2C) (arom C), 129.5 (2C), 128.3 (4C), 127.0 (4C) (arom CH), 124.7 (2C) (C-4, C-4'), 83.7 (2C) (C-2,

C-2'), 60.2 (2C), 59.6 (2C) (CH_3–O); FAB HRMS (MeOH/NBA/NaI): calcd for $C_{24}H_{22}O_8Na$ 461.1212 (M+Na); Found 461.1233.



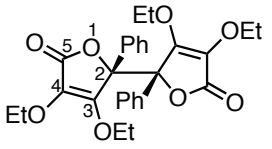
rac-**2b**

***rac*-3,3',4,4'-Tetramethoxy-2,2'-diphenyl-[2,2'-bifuran]-5,5'(2*H*,2'*H*)-dione (*rac*-2b):** colorless plates (from MeOH); mp 167-169 °C; IR ($CHCl_3$) ν 1766 (C=O), 1678 (C=C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43-7.40 (4H, m, arom H), 7.27-7.14 (6H, m, arom H), 4.22 (6H, s, CH_3–O ×2), 3.82 (6H, s, CH_3–O ×2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.3 (C=O ×2), 160.3 (2C) (C-3, C-3'), 133.6 (2C) (arom C), 129.0 (2C), 127.7 (4C), 127.3 (4C) (arom CH), 123.8 (2C) (C-4, C-4'), 83.6 (2C) (C-2, C-2'), 60.5 (2C), 60.2p (2C) (CH_3–O); FAB HRMS (MeOH/NBA): calcd for $C_{24}H_{23}O_8$ 439.1393 (M+H); Found 439.1416.



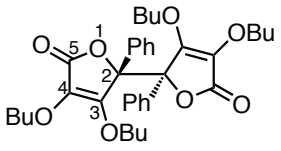
meso-**2c**

***meso*-3,3',4,4'-Tetraethoxy-2,2'-diphenyl-[2,2'-bifuran]-5,5'(2*H*,2'*H*)-dione (*meso*-2c):** colorless cubes (from CH_2Cl_2-hexane); mp 244-246 °C; IR ($CHCl_3$) ν 1762 (C=O), 1670 (C=C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88-7.83 (4H, m, arom H), 7.38-7.34 (6H, m, arom H), 4.45 (2H, dq, J = 9.9, 7.2 Hz, –CH_2–O), 4.32 (2H, dq, J = 9.9, 7.2 Hz, –CH_2–O), 3.68 (2H, dq, J = 9.9, 7.2 Hz, –CH_2–O), 3.38 (2H, dq, J = 9.9, 7.2 Hz, –CH_2–O), 1.43 (6H, t, J = 7.2 Hz, CH_3 ×2), 0.95 (6H, t, J = 7.2 Hz, CH_3 ×2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.9 (C=O ×2), 159.6(2C) (C-3, C-3'), 133.9 (2C) (arom C), 129.3 (2C), 128.1 (4C), 127.0 (4C) (arom CH), 122.8 (2C) (C-4, C-4'), 83.5 (2C) (C-2, C-2'), 68.5 (2C), 68.2 (2C) (–CH_2–O), 15.5 (2C), 14.9 (2C) (CH_3). Anal. Calcd for $C_{28}H_{30}O_8$: C, 68.00; H, 6.11. Found: C, 68.16; H, 6.32.



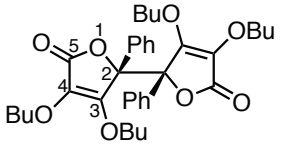
rac-**2c**

***rac*-3,3',4,4'-Tetraethoxy-2,2'-diphenyl-[2,2'-bifuran]-5,5'(2*H*,2'*H*)-dione (*rac*-2c):** colorless cubes (from MeOH); mp 242-244 °C; IR ($CHCl_3$) ν 1762 (C=O), 1670 (C=C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86-7.83 (4H, m, arom H), 7.37-7.35 (6H, m, arom H), 4.45 (2H, dq, J = 9.9, 7.2 Hz, –CH_2–O), 4.32 (2H, dq, J = 9.9, 7.2 Hz, –CH_2–O), 3.68 (2H, dq, J = 9.9, 7.2 Hz, –CH_2–O), 3.38 (2H, dq, J = 9.9, 7.2 Hz, –CH_2–O), 1.43 (6H, t, J = 7.2 Hz, CH_3 ×2), 0.95 (6H, t, J = 7.2 Hz, CH_3 ×2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.6 (C=O ×2), 159.4 (2C) (C-3, C-3'), 133.7 (2C) (arom C), 129.1 (2C), 127.9 (4C), 126.8 (4C) (arom CH), 122.7 (2C) (C-4, C-4'), 83.4 (2C) (C-2, C-2'), 68.4 (2C), 68.0 (2C) (–CH_2–O), 15.4 (2C), 14.9 (2C) (CH_3). Anal. Calcd for $C_{28}H_{30}O_8$: C, 68.00; H, 6.11. Found: C, 68.16; H, 6.32.



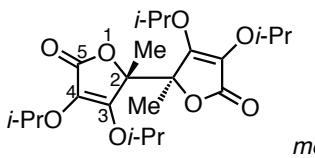
meso-**2d**

***meso*-3,3',4,4'-Tetrabutoxy-2,2'-diphenyl-[2,2'-bifuran]-5,5'(2*H*,2'*H*)-dione (*meso*-2d):** colorless needles (from CH_2Cl_2-hexane); mp 109-110 °C; IR ($CHCl_3$) ν 1762 (C=O), 1670 (C=C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87-7.80 (4H, m, arom H), 7.38-7.35 (6H, m, arom H), 4.38 (2H, dt, J = 9.9, 6.6 Hz, –$\underline{H}_aCH_b$–O ×2), 4.21 (2H, dt, J = 9.9, 6.6 Hz, –$H_a\underline{C}H_b$–O ×2), 3.60 (2H, dt, J = 9.9, 6.6 Hz, –$\underline{H}_cCH_d$–O ×2), 3.21 (2H, dt, J = 9.9, 6.6 Hz, –$H_c\underline{C}H_d$–O ×2), 1.79 (4H, quint, J = 6.6 Hz, OCH_2-$C\underline{H}_2$– ×2), 1.55 (4H, sext, J = 7.2 Hz, OCH_2CH_2–$C\underline{H}_2$– ×2), 1.32 (4H, quint, J = 6.6 Hz, OCH_2-$C\underline{H}_2$– ×2), 1.20 (4H, sext, J = 7.2 Hz, OCH_2CH_2–$C\underline{H}_2$– ×2), 1.01 (6H, t, J = 7.2 Hz, CH_3 ×2), 0.83 (6H, t, J = 7.2 Hz, CH_3 ×2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.8 ($\underline{C}$=O ×2), 159.5 (2C) (C-3, C-3'), 134.0 (2C) (arom C), 129.2 (2C), 128.1 (4C), 127.1 (4C) (arom CH), 123.2 (2C) (C-4, C-4'), 83.5 (2C) (C-2, C-2'), 72.4 (2C), 72.3 (2C) (–$\underline{C}H_2$–O), 31.7 (2C), 31.3 (2C) (OCH_2-$\underline{C}H_2$–), 19.0 (2C), 18.8 (2C) (OCH_2CH_2–$\underline{C}H_2$–), 13.8 (2C), 13.7 (2C) (CH_3). FAB HRMS (MeOH/NBA): calcd for $C_{36}H_{47}O_8$ 607.3271 (M+H); Found 607.3322.



rac-**2d**

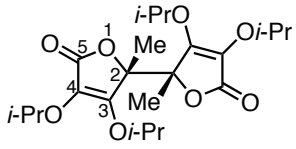
***rac*-3,3',4,4'-Tetrabutoxy-2,2'-diphenyl-[2,2'-bifuran]-5,5'(2*H*,2'*H*)-dione (*rac*-2d):** colorless needles (from MeOH); mp 105-106 °C; IR ($CHCl_3$) ν 1762 (C=O), 1670 (C=C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85-7.80 (4H, m, arom H), 7.40-7.33 (6H, m, arom H), 4.52 (4H, m, CH_2–O ×2), 4.25-4.13 (4H, m, CH_2–O ×2), 1.86-1.16 (16H, m, $C\underline{H}_2$– ×8),1.01 (6H, t, J = 7.2 Hz, CH_3 ×2), 0.83 (6H, t, J = 7.2 Hz, CH_3 ×2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.8 ($\underline{C}$=O ×2), 159.5 (2C) (C-3, C-3'), 134.0 (2C) (arom C), 129.3 (2C), 128.1 (4C), 127.5 (4C) (arom CH), 123.2 (2C) (C-4, C-4'), 83.5 (2C) (C-2, C-2'), 72.9 (2C), 72.6 (2C) (–$\underline{C}H_2$–O), 31.9 (2C), 31.5 (2C) (OCH_2-$\underline{C}H_2$–), 19.0 (2C), 18.9 (2C) (OCH_2CH_2–$\underline{C}H_2$–), 13.8 (2C), 13.7 (2C) (CH_3). FAB HRMS (MeOH/NBA): calcd for $C_{36}H_{47}O_8$ 607.3271 (M+H); Found 607.3322.



meso-**2e**

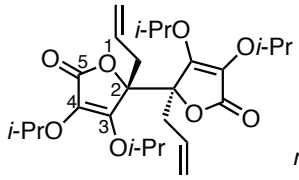
***meso*-3,3',4,4'-Tetraisopropoxy-2,2'-dimethyl-[2,2'-bifuran]-5,5'(2*H*,2'*H*)-dione (*meso*-2e):** R_f = 0.42 (Et_2O/hexane 6:4 v/v); colorless oil; IR ($CHCl_3$) ν 1755 (C=O), 1670 (C=C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.17 (2H, sept, J = 6.1 Hz, >CH-O ×2), 4.83 (2H, sept, J = 6.1 Hz, >CH-O ×2), 1.58 (6H, s, CH_3 ×2), 1.32 (6H, d, J = 6.1 Hz, CH_3 ×2), 1.30 (6H, d, J = 6.1 Hz, CH_3 ×2), 1.27 (6H, d, J = 6.1 Hz, CH_3 ×2), 1.24 (6H, d, J = 6.1 Hz, CH_3 ×2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.6 (2C) (C=O), 160.1 (2C) (C-3, C-3'),

118.6 (2C) (C-4, C-4'), 81.3 (2C) (C-2, C-2'), 74.8 (2C), 73.1 (2C) (>CH-O), 22.53 (2C), 22.51 (2C), 22.44 (2C), 22.38 (2C), 19.8 (2C) (CH_3); FAB MS *m/z* (rel intensity), 427 (M^++H, 100), 385 (12), 283 (14), 214 (36), 171 (80), 129 (36); FAB HRMS (MeOH/NBA): calcd for $C_{22}H_{35}O_8$ 427.2332 (M+H); Found 427.2398.

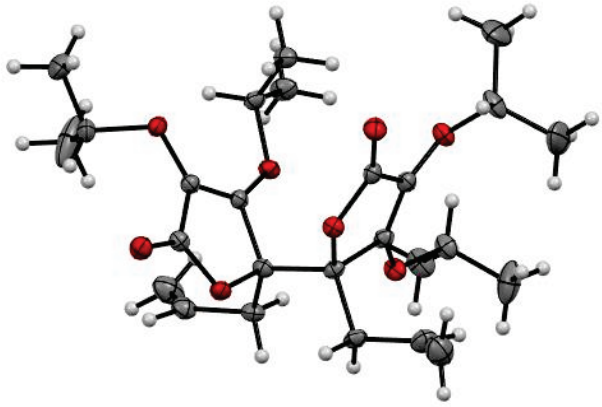


rac-**2e**

***rac*-3,3',4,4'-Tetraisopropoxy-2,2'-dimethyl-[2,2'-bifuran]-5,5'(2*H*,2'*H*)-dione (*rac*-2e):** R_f = 0.56, 0.24 (Et_2O/hexane 6:4 v/v); colorless oil; IR ($CHCl_3$) *v* 1762 (C=O), 1677 (C=C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.03 (1H, sept, *J* = 6.1 Hz, >CH-O), 4.88 (1H, sept, *J* = 6.1 Hz, >CH-O), 4.38 (1H, sept, *J* = 6.1 Hz, >CH-O), 3.86 (1H, sept, *J* = 6.1 Hz, >CH-O), 1.98 (3H, s, CH_3), 1.68 (3H, s, CH_3), 1.29 (3H, d, *J* = 6.1 Hz, CH_3), 1.29 (3H, d, *J* = 6.1 Hz, CH_3), 1.27 (3H, d, *J* = 6.1 Hz, CH_3), 1.25 (3H, d, *J* = 6.1 Hz, CH_3), 1.23 (3H, d, *J* = 6.1 Hz, CH_3), 1.22 (3H, d, *J* = 6.1 Hz, CH_3), 1.19 (3H, d, *J* = 6.1 Hz, CH_3), 1.18 (3H, d, *J* = 6.1 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.6, 168.8 (C=O), 158.1, 139.9 (C-3, C-3'), 132.9, 118.4 (C-4, C-4'), 83.3, 79.1 (C-2, C-2'), 74.7, 73.2, 72.8, 70.1 (>CH-O), 23.7, 23.3, 22.5, 22.5, 22.4, 22.2, 22.0, 21.9, 18.0, 11.0 (CH_3). FAB HRMS (MeOH/NBA): calcd for $C_{22}H_{35}O_8$ 427.2332 (M+H); Found 427.2398.



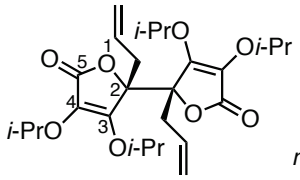
meso-**2f**



Crystal structure of *meso*-**2f**

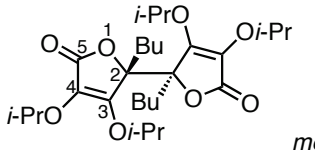
***meso*-2,2'-Diallyl-3,3',4,4'-tetraisopropoxy-[2,2'-bifuran]-5,5'(2*H*,2'*H*)-dione (*meso*-2f):** R_f = 0.38 (Et_2O/hexane 5:5 v/v); yellow plates (from Et_2O-hexane); mp 98-99 °C; IR ($CHCl_3$) *v* 1762 (C=O), 1670 (C=C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.61-5.45 (2H, m, -CH= ×2), 5.20-5.11 (6H, m, >CH-O ×2, $=CH_2$ ×2), 4.88 (2H, sept, *J* = 6.1 Hz, >CH-O ×2), 2.73 (4H, d, *J* = 7.2 Hz, $-CH_2-$ ×2), 1.34 (6H, d, *J* = 6.1 Hz, CH_3 ×2), 1.30 (6H, d, *J* = 6.1 Hz, CH_3 ×2), 1.26 (6H, d, *J* = 6.1 Hz, CH_3 ×2), 1.21 (6H, d, *J* = 6.1 Hz, 2 CH_3 ×2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.2 (2C) (C=O), 155.6 (2C) (C-3, C-3'), 129.6 (2C) (-CH=), 120.5 (2C) ($=CH_2$), 120.1 (2C) (C-4, C-4'), 83.6 (2C) (C-2, C-2'), 74.6 (2C), 72.7 (2C) (>CH-O), 35.0 (2C) (CH_2), 22.8 (2C), 22.6 (2C), 22.4 (2C), 22.2 (2C) (CH_3); FAB HRMS (MeOH/NBA): calcd for $C_{26}H_{39}O_8$ 479.2645 (M+H); Found 479.2651. X-Ray crystallographic data: space group *P*c (#7);

monoclinic; a = 10.4615(3), b = 9.2344(3), c = 14.4997(5) Å, β = 105.720(2)°, V = 1348.37(7) Å^3, Z = 2; R = 0.043; R_w = 0.119; GOF = 0.95. X-Ray coordinates were deposited with the Cambridge Crystallographic Data Centre: *meso*-**2f**: CCDC 1866647.



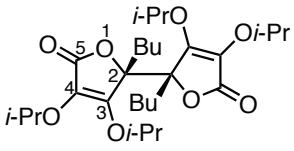
rac-**2f**

***rac*-2,2'-Diallyl-3,3',4,4'-tetraisopropoxy-[2,2'-bifuran]-5,5'(2*H*,2'*H*)-dione (*rac*-2f):** R_f = 0.55, 0.45 (Et_2O/hexane 5:5 v/v); yellow oil; IR ($CHCl_3$) ν 1761 (C=O), 1676 (C=C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.84-5.71 (1H, m, -CH=), 5.60-5.46 (1H, m, -CH=), 5.21-5.07 (4H, m, =CH_2 ×2), 5.00 (1H, sept, J = 6.1 Hz, >CH-O), 4.84 (1H, sept, J = 6.1 Hz, >CH-O), 4.40 (1H, sept, J = 6.1 Hz, >CH-O), 3.85 (1H, sept, J = 6.1 Hz, >CH-O), 3.17 (1H, dd, J = 15.8, 6.6 Hz, -$\underline{H_a}CH_b$-), 3.04 (2H, d, J = 7.2 Hz, -CH_2-), 3.01 (1H, dd, J = 15.8, 6.6 Hz, -$H_aC\underline{H_b}$-), 1.29 (3H, d, J = 6.1 Hz, CH_3), 1.26 (3H, d, J = 6.1 Hz, CH_3), 1.25 (3H, d, J = 6.1 Hz, CH_3), 1.22 (3H, d, J = 6.1 Hz, CH_3), 1.21 (3H, d, J = 6.1 Hz, CH_3), 1.19 (3H, d, J = 6.1 Hz, CH_3), 1.18 (3H, d, J = 6.1 Hz, CH_3), 1.17 (3H, d, J = 6.1 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.6, 169.1 (C=O), 155.5, 141.5 (C-3, C-3'), 133.0, 119.8 (C-4, C-4'), 131.4, 130.2 (-CH=), 120.5, 118.5 (=CH_2), 85.0, 81.8 (C-2, C-2'), 75.1, 73.4, 72.8, 70.4 (>CH-O), 32.7, 29.6 (CH_2), 23.7, 23.3, 22.8, 22.6, 22.5, 22.3, 22.1, 22.0 (CH_3); FAB MS (MeOH/NBA) *m/z* (rel intensity) 479 (M^++H, 28), 335 (12), 239 (66), 197 (100), 155 (30).



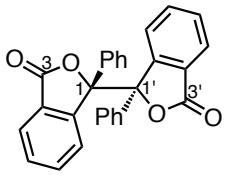
meso-**2g**

***meso*-2,2'-Dibutyl-3,3',4,4'-tetraisopropoxy-[2,2'-bifuran]-5,5'(2*H*,2'*H*)-dione (*meso*-2g):** R_f = 0.65 (Et_2O/hexane 6:4 v/v); colorless plates (from Et_2O-hexane); mp 81-82 °C; IR ($CHCl_3$) ν 1760 (C=O), 1670 (C=C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.18 (2H, sept, J = 6.1 Hz, >CH-O ×2), 4.92 (2H, sept, J = 6.1 Hz, >CH-O ×2), 2.00-1.85 (4H, m, CH_2 ×2), 1.35-1.21 (8H, m, CH_2 ×4), 1.34 (6H, d, J = 6.1 Hz, CH_3 ×2), 1.31 (6H, d, J = 6.1 Hz, CH_3 ×2), 1.27 (6H, d, J = 6.1 Hz, CH_3 ×2), 1.24 (6H, d, J = 6.1 Hz, CH_3 ×2), 0.87 (6H, t, J = 7.2 Hz, CH_3 ×2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.8 (2C) (C=O), 156.2 (2C) (C-3, C-3'), 119.9 (2C) (C-4, C-4'), 84.9 (2C) (C-2, C-2'), 74.6 (2C), 72.4 (2C) (>CH-O), 30.0 (2C), 24.2 (2C), 22.6 (2C) (CH_2), 22.9 (2C), 22.8 (2C), 22.6 (2C), 22.5 (2C), 14.0 (2C) (CH_3); FAB MS *m/z* (rel intensity) 511 (M^++H, 24), 325 (20), 213 (100), 171 (30); FAB HRMS (MeOH/NBA): calcd for $C_{28}H_{47}O_8$ 511.3271 (M+H); Found 511.3260.

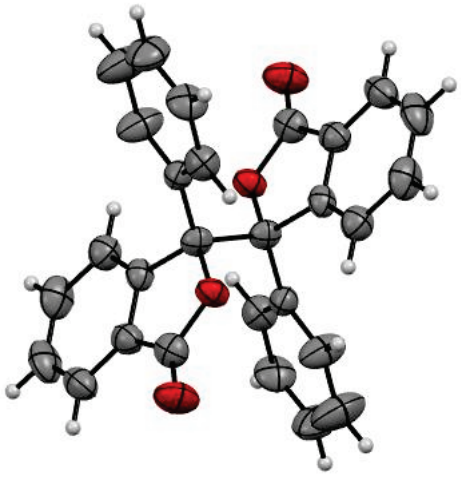


rac-**2g**

***rac*-2,2'-Dibutyl-3,3',4,4'-tetraisopropoxy-[2,2'-bifuran]-5,5'(2*H*,2'*H*)-dione (*rac*-2g):** R_f = 0.80, 0.70 (Et_2O/hexane 6:4 v/v); colorless oil; IR ($CHCl_3$) ν 1759 (C=O), 1676 (C=C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.03 (1H, sept, J = 6.1 Hz, >CH-O), 4.88 (1H, sept, J = 6.1 Hz, >CH-O), 4.38 (1H, sept, J = 6.1 Hz, >CH-O), 3.86 (1H, sept, J = 6.1 Hz, >CH-O), 2.46-2.17 (4H, m, CH_2 ×2), 1.40-1.15 (32H, m, CH_2 ×4, CH_3 ×8), 0.93 (3H, t, J = 7.2 Hz, CH_3), 0.87 (3H, t, J = 7.2 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.7, 169.2 (C=O), 155.6, 144.3 (C-3, C-3'), 132.4, 119.6 (C-4, C-4'), 85.9, 81.9 (C-2, C-2'), 74.8, 73.1, 72.6, 70.0 (>CH-O), 28.3, 27.3, 24.5, 23.8, 22.5 (2C) (CH_2), 23.6, 23.1, 22.4 (3C), 22.2, 22.0, 21.9, 14.0, 13.7 (CH_3); FAB MS (MeOH/NBA) *m/z* (rel intensity) 511 (M^++H, 98), 469 (8), 343 (12), 213 (100); FAB HRMS (MeOH/NBA): calcd for $C_{28}H_{47}O_8$ 511.3271 (M+H); Found 511.3300.

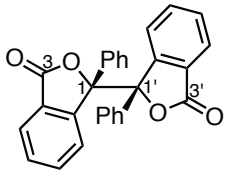


meso-**2h**



Crystal structure of *meso*-**2h**

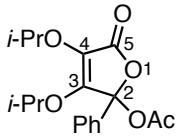
***meso*-1,1'-Diphenyl-[1,1'-biisobenzofuran]-3,3'(1*H*,1'*H*)-dione (*meso*-2h):** R_f = 0.47 ($CHCl_3$); colorless microcrystals (from CH_2Cl_2/hexane); mp 291-292 °C (lit,[19e] mp 289-290 °C); IR (KBr) ν 1773 (COO); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.36 (2H, d, J = 7.8 Hz, arom H), 7.73 (2H, t, J = 7.5 Hz, arom H), 7.64-7.57 (6H, m, arom H), 7.41 (2H, t, J = 7.5 Hz, arom H), 7.13-7.09 (6H, m, arom H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.0 (COO), 149.3, 135.2, 126.4 (arom C), 134.4, 129.9, 128.7, 128.0, 127.0, 125.7, 125.3 (arom CH), 90.2 (C-O); FAB HRMS (MeOH/NBA): calcd for $C_{28}H_{19}O_4$ 419.1283 (M+H); Found 419.1289. X-Ray crystallographic data[29]: space group $P2_1/a$ (#14); monoclinic; a = 9.803(4), b = 14.011(7), c = 7.596(4) Å, β = 98.14(3)°, V = 1032.8(8) Å^3, Z = 4; R = 0.0426; R_w = 0.0840; GOF = 0.698. X-Ray coordinates were deposited with the Cambridge Crystallographic Data Centre: **2h**: CCDC 1866646.



rac-**2h**

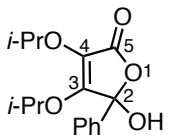
***rac*-1,1'-Diphenyl-[1,1'-biisobenzofuran]-3,3'(1*H*,1'*H*)-dione (*rac*-2h)[19]:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (2H, d, J = 7.8 Hz, arom H), 7.73 (2H, t, J = 7.5 Hz, arom H), 7.64-7.53 (6H, m, arom H), 7.36 (2H, t, J = 7.5 Hz, arom H), 7.22-7.20 (6H, m, arom H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.5 (C=O), 149.2, 136.9, 126.6 (arom C), 134.8, 130.0, 128.6, 128.3, 128.0, 125.8, 124.7 (arom CH), 91.0 (C-O).

Reaction of 2,3-Dialkoxy-4-hydroxycyclobut-2-en-1-ones 1a-h under High Dilution Conditions. 2,3-Dialkoxy-4-hydroxycyclobut-2-en-1-one **1** (0.5 mmol) was dissolved in AcOH (250 mL for **1a-d**, 100 mL for **1e-h**), and $Mn(OAc)_3$•$2H_2O$ (2.0 mmol) was added to the solution. The mixture was heated under reflux using an oil bath at 140 °C until the Mn(III) oxidant was completely consumed. The existence of the Mn(III) was monitored by iodine-starch paper and each reaction time is listed in Table 1. After completion of the reaction, the solvent was removed in vacuo and water (10 mL) was added to the residue. The obtained aqueous mixture was extracted with $CHCl_3$ (10 mL × 5), and the combined extracts were washed with water (10 mL), a saturated aqueous solution of $NaHCO_3$ (10 mL), brine (10 mL), dried over anhydrous magnesium sulfate (3 g), then concentrated to dryness. The residue was separated by column chromatography on silica gel eluting with $CHCl_3$, mainly giving the corresponding 4-acetoxy-2-buten-4-olide **3** (Table 1). In order to further characterize the acetate **3**, the acetate **3** underwent hydrolysis in AcOH (5 mL)/water (10 mL) at reflux temperature, and the corresponding 4-hydroxy-2-buten-4-olide **3'** was obtained after separation by preparative silica gel TLC developing with Et_2O/hexane (5:5 v/v).



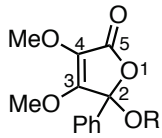
3a

3,4-Diisopropoxy-5-oxo-2-phenyl-2,5-dihydrofuran-2-yl acetate (3a): yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54-7.40 (2H, m, arom H), 7.39-7.38 (3H, m, arom H), 5.15 (1H, sept, J = 6.1 Hz, >CH-O), 4.89 (1H, sept, J = 6.1 Hz, >CH-O), 2.15 (3H, s, OAc), 1.32 (3H, d, J = 6.1 Hz, CH_3), 1.31 (3H, d, J = 6.1 Hz, CH_3), 1.26 (3H, d, J = 6.1 Hz, CH_3), 1.09 (3H, d, J = 6.1 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.1, 167.3 (C=O), 156.0 (C-3), 135.7 (arom C), 129.7, 128.5 (2C), 125.6 (2C) (arom CH), 120.2 (C-4), 99.1 (C-2), 75.3, 74.0 (>CH-O), 22.6 (Ac), 22.5 (2C), 22.1, 21.6 (CH_3).



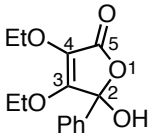
3a'

5-Hydroxy-3,4-diisopropoxy-5-phenylfuran-2(5*H*)-one (3a'): Yield 25%; colorless blocks (from CH_2Cl_2/hexane); mp 126 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58-7.55 (2H, m, arom H), 7.39-7.38 (3H, m, arom H), 5.10 (1H, sept, J = 6.1 Hz, >CH-O), 4.87 (1H, sept, J = 6.1 Hz, >CH-O), 4.16 (1H, Br. s, OH), 1.33 (3H, d, J = 6.1 Hz, CH_3), 1.30 (3H, d, J = 6.1 Hz, CH_3), 1.26 (3H, d, J = 6.1 Hz, CH_3), 1.10 (3H, d, J = 6.1 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.1 (C=O), 157.2 (C-3), 137.1 (arom C), 129.6, 128.6 (2C), 126.0 (2C) (arom CH), 119.1 (C-4), 99.4 (C-2), 75.0, 73.9 (>CH-O), 22.7 (3C), 22.3 (CH_3); FAB HRMS (MeOH/NBA): calcd for $C_{16}H_{21}O_5$ 293.1389 (M+H); Found 293.1391.



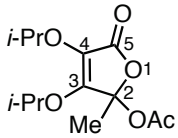
3b : R = Ac
3b': R = H

3,4-Dimethoxy-5-oxo-2-phenyl-2,5-dihydrofuran-2-yl acetate (3b)[11a,11c,22]**:** The products **3b** and the alcohol, 5-hydroxy-3,4-dimethoxy-5-phenylfuran-2(5*H*)-one (**3b'**), could not be isolated by chromatographic separation (**3b**:**3b'** = *ca.* 2:3). Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60-7.30 (5H, m, arom H), 4.10 (3H, s, OCH_3), 3.89 (3H, s, OCH_3), 2.16 (3H, s, OAc); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.4 (2C),167.3 (C=O, C-3), 160.3, 160.2 (C=O, C-3), 133.6, 133.5 (arom C), 129.5, 129.0, 128.3 (2C), 127.7 (2C), 127.3 (2C), 126.9 (2C) (arom CH), 124.7, 123.8 (C-4), 83.7, 83.6 (C-2), 60.5, 60.3, 60.2, 59.4 (CH_3), 21.7 (Ac).



3c'

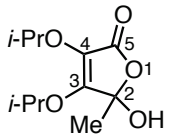
3,4-Diethoxy-5-hydroxy-5-phenylfuran-2(5*H*)-one (3c')[11a,11c]**:** yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46-7.43 (2H, m, arom H), 7.22-7.12 (3H, m, aromH), 4.54 (2H, q, J = 7.2 Hz, OCH_2), 4.04 (2H, m, OCH_2), 1.46 (3H, t, J = 7.2 Hz, CH_3), 1.30 (1H, br. OH), 1.28 (3H, t, J = 7.2, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.8 (C=O), 159.6 (C-3), 134.2 (arom C), 128.8, 127.6 (2C), 127.3 (2C) (arom CH), 122.3 (C-4), 83.4 (C-2), 69.0, 68.5 ($\underline{C}H_2$-O), 15.3, 15.2 (CH_3).



3e

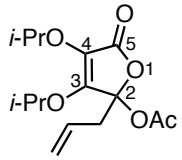
3,4-Diisopropoxy-2-methyl-5-oxo-2,5-dihydrofuran-2-yl acetate (3e): R_f = 0.60 (Et_2O/hexane 6:4 v/v); colorless oil; IR ($CHCl_3$) ν 1770 (C=O), 1683 (>C=C<); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.20 (1H, sept, J = 6.1 Hz, >CH-O), 4.86 (1H, sept, J = 6.1 Hz, >CH-O), 2.05 (3H, s, $COCH_3$), 1.66 (3H, s, CH_3), 1.34 (3H, d, J = 6.1 Hz, CH_3), 1.31 (3H, d, J = 6.1 Hz, CH_3), 1.30 (3H, d, J = 6.1 Hz, CH_3), 1.28 (3H, d, J = 6.1 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.1, 166.9 ($\underline{C}OCH_3$, C-5), 155.8 (C-3), 119.7 (C-4), 99.2 (C-2), 74.9, 73.8 (>CH-O), 23.8, 22.58, 22.56, 22.46, 22.43 (CH_3), 21.5 ($CO\underline{C}H_3$); MS *m/z* (rel intensity) 273

(M^++1, 16), 213 (52), 171 (100), 129 (26); FAB HRMS (acetone/NBA): calcd for $C_{13}H_{21}O_6$ (M+H) 273.1338; Found 273.1332.



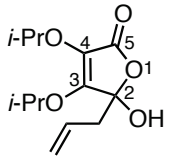
3e'

5-Hydroxy-3,4-diisopropoxy-5-methylfuran-2(5H)-one (3e'): R_f = 0.33 (Et_2O/hexane 7:3 v/v); colorless needles (from Et_2O/hexane); mp 118 °C; IR ($CHCl_3$) *v* 3306 (OH), 1759 (C=O), 1678 (>C=C<); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.17 (1H, sept, *J* = 6.1 Hz, >CH-O), 4.80 (1H, sept, *J* = 6.1 Hz, >CH-O), 3.71 (1H, s, OH), 1.65 (3H, s, CH_3), 1.36 (3H, d, *J* = 6.1 Hz, CH_3), 1.34 (3H, d, *J* = 6.1 Hz, CH_3), 1.27 (3H, d, *J* = 6.1 Hz, CH_3), 1.26 (3H, d, *J* = 6.1 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.0 (C-5), 157.2 (C-3), 118.5 (C-4), 99.1 (C-2), 74.7, 73.6 (>CH-O), 23.7, 22.5 (2C), 22.4 (2C) (CH_3).



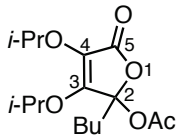
3f

2-Allyl-3,4-diisopropoxy-5-oxo-2,5-dihydrofuran-2-yl acetate (3f): R_f = 0.50 (Et_2O/hexane 5:5 v/v); yellow oil; IR ($CHCl_3$) *v* 1767 (C=O), 1682 (>C=C<); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.64-5.45 (1H, m, -CH=), 5.15-5.09 (3H, m, >CH-O, $=CH_2$), 4.78 (1H, sept, *J* = 6.1 Hz, >CH-O), 2.73 (1H, dd, *J* = 14.2, 6.4 Hz, -C$\underline{H}_{1a}H_{1b}$-), 2.51 (1H, dd, *J* = 14.2, 7.9 Hz, -$CH_{1a}\underline{H}_{1b}$-), 1.98 (3H, s, $COCH_3$), 1.25 (3H, d, *J* = 6.1 Hz, CH_3), 1.23 (3H, d, *J* = 6.1 Hz, CH_3), 1.20 (3H, d, *J* = 6.1 Hz, CH_3), 1.18 (3H, d, *J* = 6.1 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.9, 166.8 ($\underline{C}OCH_3$, C-5), 153.9 (C-3), 128.6 (-CH=), 121.0 ($=CH_2$), 120.4 (C-4), 99.8 (C-2), 74.7, 73.4 (>CH-O), 40.0 (CH_2), 22.5, 22.4, 22.3, 22.2 (CH_3), 21.3 ($CO\underline{C}H_3$).



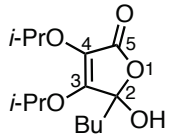
3f'

5-Allyl-5-hydroxy-3,4-diisopropoxyfuran-2(5*H*)-one (3f'): Yield 19%; R_f = 0.21 (Et_2O/hexane 5:5 v/v); yellow oil; IR ($CHCl_3$) *v* 3333 (OH), 1761 (C=O), 1679 (>C=C<); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.80-5.67 (1H, m, -CH=), 5.25 (1H, d, *J* = 15.8 Hz, $=C\underline{H}_{trans}H_{cis}$), 5.21 (1H, d, *J* = 11.2 Hz, $=CH_{trans}\underline{H}_{cis}$), 5.13 (1H, sept, *J* = 6.1 Hz, >CH-O), 4.82 (1H, sept, *J* = 6.1 Hz, >CH-O), 3.74 (1H, s, OH), 2.68 (1H, dd, *J* = 13.6, 7.2 Hz, -C$\underline{H}_{1a}H_{1b}$-), 2.63 (1H, dd, *J* = 13.6, 7.2 Hz, -$CH_{1a}\underline{H}_{1b}$-), 1.35 (6H, d, *J* = 6.1 Hz, CH_3 ×2), 1.26 (6H, d, *J* = 6.1 Hz, CH_3 ×2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.7 (C-5), 155.8 (C-3), 130.5 (-CH=), 121.5 ($=CH_2$), 119.5 (C-4), 99.5 (C-2), 74.8, 73.5 (>CH-O), 40.9 (CH_2), 22.6 (2C), 22.4 (2C) (CH_3); MS *m/z* (rel intensity) 257 (M^++H, 100), 239 (40), 173 (70), 127 (26); FAB HRMS (acetone/NBA): calcd for $C_{13}H_{21}O_5$ (M+H) 257.1389; Found 257.1372.



3g

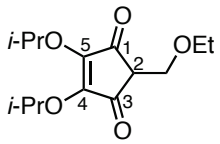
2-Butyl-3,4-diisopropoxy-5-oxo-2,5-dihydrofuran-2-yl acetate (3g): R_f = 0.62 (Et_2O/hexane 5:5 v/v); colorless oil; IR ($CHCl_3$) *v* 1770 (C=O), 1682 (>C=C<); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.19 (1H, sept, *J* = 6.1 Hz, >CH-O), 4.88 (1H, sept, *J* = 6.1 Hz, >CH-O), 2.05 (3H, s, $COCH_3$), 1.83-1.74 (2H, m, CH_2), 1.40-1.24 (4H, m, CH_2 ×2), 1.33 (3H, d, *J* = 6.1 Hz, CH_3), 1.30 (6H, d, *J* = 6.1 Hz, CH_3 ×2), 1.27 (3H, d, *J* = 6.1 Hz, CH_3), 0.90 (3H, t, *J* = 6.1 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.2, 167.2 ($\underline{C}OCH_3$, C-5), 154.6 (C-3), 120.4 (C-4), 101.0 (C-2), 74.8, 73.7 (>CH-O), 35.7, 24.0 (CH_2), 22.6 (2C), 22.5 (2C) (CH_3), 22.4 (CH_2), 21.6 ($CO\underline{C}H_3$), 13.9 (CH_3).



3g'

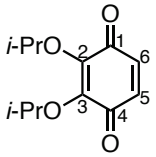
5-Butyl-5-hydroxy-3,4-diisopropoxyfuran-2(5*H*)-one (3g'): Yield 23%; R_f = 0.29 (Et_2O/hexane 5:5 v/v); colorless oil; IR ($CHCl_3$) *v* 3356 (OH), 1760 (C=O), 1678 (>C=C<); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.17 (1H, sept, *J* = 6.1 Hz, >CH-O), 4.81 (1H, sept, *J* = 6.1 Hz, >CH-O), 3.94 (1H, s, OH), 1.99-1.81 (2H, m, CH_2), 1.47-1.25 (4H, m, CH_2 ×2), 1.36 (3H, d, *J* = 6.1 Hz, CH_3), 1.34 (3H, d, *J* = 6.1 Hz, CH_3), 1.29 (3H, d, *J* = 6.1 Hz, CH_3), 1.24 (3H, d, *J* = 6.1 Hz, CH_3), 0.89 (3H, t, *J* = 6.6 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.4 (C-5), 156.4 (C-3), 119.0 (C-4), 101.0 (C-2), 74.7, 73.5 (>CH-O), 35.6, 25.0, 22.4 (CH_2), 22.6, 22.5, 22.4 (2C), 13.9 (CH_3); MS *m/z* (rel intensity) 273 (M^++H, 60), 255 (50), 189 (100), 143 (24); FAB HRMS (acetone/NBA): calcd for $C_{14}H_{25}O_5$ (M+H) 273.1702; Found 273.1696.

Oxidation of Squarates 1i-l Having a C–C Unsaturated Substituent under Mn(III)-Cu(II) System. A typical procedure is as follows. To a squarate **1** (0.5 mmol) in EtOH (10 mL), $Mn(OAc)_3$ (0.5 mmol) and $Cu(OAc)_2$ (0.5 mmol) were added, and the mixture was stirred at room temperature under argon. After the Mn(III) oxidant was completely consumed (see in Table 2), the solvent was removed in vacuo and water (10 mL) was added. The aqueous mixture was extracted with $CHCl_3$ (10 mL × 5), and the combined extracts were washed with a saturated aqueous solution of $NaHCO_3$ (10 mL), brine (10 mL), dried over anhydrous magnesium sulfate (3 g), then concentrated to dryness. The residue was separated by column chromatography on silica gel eluting with EtOAc/hexane, giving the products listed in Table 2.



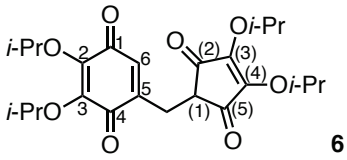
4i

2-(Ethoxymethyl)-4,5-diisopropoxycyclopent-4-ene-1,3-dione (4i): R_f = 0.57 (6:4 Et_2O-hexane); colorless oil; IR ($CHCl_3$) ν 1686 (C=O), 1609 (>C=C<); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.46 (2H, sept, J = 6.1 Hz, >CH-O ×2), 3.82 (2H, d, J = 3.0 Hz, CH_2), 3.40 (2H, q, J = 7.0 Hz, CH_2), 2.71 (1H, t, J = 3.0 Hz, >CH-), 1.35 (6H, d, J = 6.1 Hz, CH_3 ×2), 1.33 (6H, d, J = 6.1 Hz, CH_3 ×2), 1.06 (3H, t, J = 7.0 Hz, CH_3); MS *m/z* (rel intensity) 271 (M^++H, 36), 149 (100), 57 (38); FAB HRMS (acetone/NBA): calcd for $C_{14}H_{23}O_5$ (M+H) 271.1545; Found 271.1543.



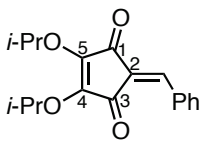
5

2,3-Diisopropoxycyclohexa-2,5-diene-1,4-dione (5)[30]**:** R_f = 0.69 (Et_2O/hexane 6:4 v/v); orange oil; IR ($CHCl_3$) ν 1757 (C=O), 1655 (>C=C<), 1585; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.61 (2H, s, -CH= ×2), 4.83 (2H, sept, J = 6.1 Hz, >CH-O ×2), 1.32 (12H, d, J = 6.1 Hz, CH_3 ×4); ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.2 (2C) (C-1, C-4), 146.1 (2C) (C-2, C-3), 135.0 (2C) (C-5, C-6), 76.3 (2C) (>CH-O), 22.7 (4C) (CH_3); MS *m/z* (rel intensity) 225 (M^++H, 10), 221 (26), 207 (30), 147 (66), 73 (100); FAB HRMS (Et_2O/NBA): calcd for $C_{12}H_{17}O_4$ (M+H) 225.1127; Found 225.1115.



6

5-((3,4-Diisopropoxy-2,5-dioxocyclopent-3-en-1-yl)methyl)-2,3-diisopropoxycyclohexa-2,5-diene-1,4-dione (6): R_f = 0.55 (Et_2O/hexane 6:4 v/v); orange oil; IR ($CHCl_3$) ν 1686 (C=O), 1655 (>C=C<); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.45 (1H, t, J = 1.2 Hz, -CH=), 5.40 (2H, sept, J = 6.1 Hz, >CH-O ×2), 4.85 (1H, sept, J = 6.1 Hz, >CH-O), 4.74 (1H, sept, J = 6.1 Hz, >CH-O), 3.13 (1H, t, J = 7.7 Hz, >CH-), 2.76 (2H, dd, J = 7.7, 1.2 Hz, CH_2), 1.33 (12H, d, J = 6.1 Hz, CH_3 ×2), 1.31 (12H, d, J = 6.1 Hz, CH_3 ×2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.7 (2C) (C=O), 184.9, 184.6 (C-1, C-4), 150.4 (C-5), 146.1, 145.9 (C-2, C-3), 144.1 (2C) (>C=C<), 132.4 (C-6), 76.2, 76.1, 74.8 (2C) (>CH-O), 48.0 (>CH-), 27.0 (CH_2), 23.0 (2C), 22.9 (2C), 22.7 (4C) (CH_3); MS *m/z* (rel intensity) 449 (M^++H, 59), 407 (22), 281 (100), 183 (70); FAB HRMS (acetone/NBA): calcd for $C_{24}H_{33}O_8$ (M+H) 449.2175; Found 449.2174.

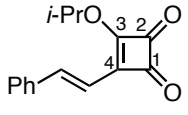


4j

2-Benzylidene-4,5-diisopropoxycyclopent-4-ene-1,3-dione (4j): R_f = 0.50 ($CHCl_3$); yellow oil; IR ($CHCl_3$) ν 1672 (C=O), 1632 (>C=C<); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 (2H, m, arom H), 7.43 (3H, m, arom H), 7.36 (1H, s, -CH=), 5.60 (1H, sept, J = 6.1 Hz, >CH-O), 5.54 (1H, sept, J = 6.1 Hz, >CH-O),

1.39 (12H, d, J = 6.1 Hz, CH_3 ×4); ^{13}C NMR (75 MHz, $CDCl_3$) δ 187.0, 185.2 (C-1, C-3), 152.4, 148.8 (C-4, C-5), 137.2 (-CH=), 133.3 (arom C), 133.0 (2C), 131.6, 128.7 (2C) (arom CH), 126.2 (C-2), 75.0, 74.9 (>CH-O), 23.1 (4C) (CH_3); MS *m/z* (rel intensity) 301 (M^++H, 8), 217 (22), 149 (46), 69 (100); FAB HRMS (acetone/NBA): calcd for $C_{18}H_{21}O_4$ (M+H) 301.1440; Found 301.1431.

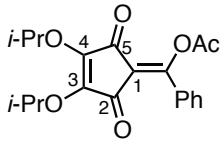
The reaction of **1k** with $Mn(pic)_3$ was as follows. To a solution of **1k** (124.0 mg; 0.41 mmol) in DMF (10 mL), $Mn(pic)_3$ (356.4 mg; 0.85 mmol) was added and the mixture was heated at 80 °C for 1.5 h. After cooling, 2 M HCl (50 mL) was added and the aqueous solution was extracted with $CHCl_3$ (10 mL ×5). The combined extracts were washed with a saturated aqueous solution of $NaHCO_3$ (10 mL), brine (10 mL), dried over anhydrous magnesium sulfate (3 g), then concentrated to dryness. The residue was separated by column chromatography on silica gel eluting with EtOAc/hexane (5:95 v/v), giving **4j** (49.7 mg; 40% yield).



7

(*E*)-3-Isopropoxy-4-styrylcyclobut-3-ene-1,2-dione (7)[31]: R_f = 0.35 ($CHCl_3$); yellow plates; mp 75-77 °C; IR ($CHCl_3$) ν 1784, 1744 (C=O), 1611 (>C=C<); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (1H, d, J = 16.2 Hz, -CH=), 7.56-7.53 (2H, m, arom H), 7.38-7.36 (3H, m, arom H), 6.96 (1H, d, J = 16.2 Hz, -CH=), 5.47 (1H, sept, J = 6.1 Hz, >CH-O), 1.51 (6H, d, J = 6.1 Hz, CH_3 ×2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.0, 192.9, 191.9 (C-1, C-2, C-3), 173.5 (C-4), 141.7 (-CH=), 135.1 (arom C), 130.3, 128.8 (2C), 127.9 (2C) (arom CH), 112.7 (-CH=), 79.4 (>CH-O), 22.5 (2C) (CH_3).

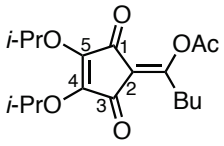
Styrylcyclobutenone **1j** (2.00 g) was dissolved in AcOH (15 mL) and the mixture was heated under reflux for 30 min. After cooling, water (30 mL) was added and the aqueous solution was extracted with $CHCl_3$ (20 mL ×3). The combined extracts were washed with water (30 mL), a saturated aqueous solution of $NaHCO_3$ (30 mL), dried over anhydrous magnesium sulfate (3 g), then concentrated to dryness, giving the rearrangement product **7** (1.60 g; quantitative yield).



4k

(3,4-Diisopropoxy-2,5-dioxocyclopent-3-en-1-ylidene)(phenyl)methyl acetate (4k): R_f = 0.26 ($CHCl_3$); yellow needles; mp 105-106 °C; IR ($CHCl_3$) ν 1776, 1674 (C=O), 1632 (>C=C<); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61-7.59 (2H, m, arom H), 7.49-7.32 (3H, m, arom H), 5.47 (2H, sept, J = 6.1 Hz, >CH-O), 2.37 (3H, s, $COCH_3$), 1.37 (6H, d, J = 6.1 Hz, CH_3 ×2), 1.33 (6H, d, J = 6.1 Hz, CH_3 ×2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.4, 183.7 (C-2, C-5), 168.3 ($\underline{C}OCH_3$), 154.3 (>C=), 150.3, 149.2 (C-3, C-4), 132.4 (arom C), 131.7, 130.1 (2C), 128.0 (2C) (arom CH), 116.2 (C-1), 74.98, 74.96 (>CH-O), 23.1 (2C), 23.0

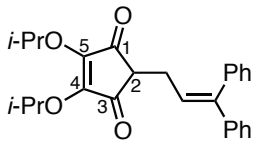
(2C) (CH_3), 21.0 ($CO\underline{C}H_3$); MS *m/z* (rel intensity) 359 (M^++H, 26), 317 (100), 233 (80), 105 (34); FAB HRMS (acetone/NBA): calcd for $C_{20}H_{23}O_6$ (M+H) 359.1495; Found 359.1495.



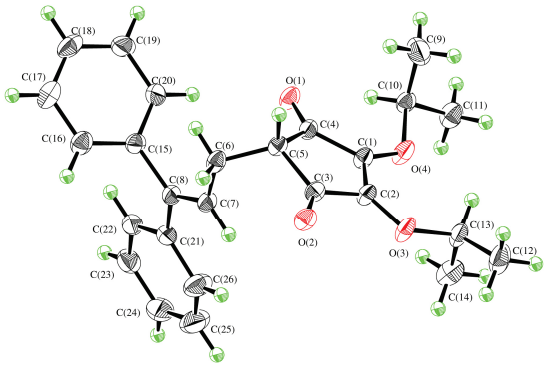
4l

1-(3,4-Diisopropoxy-2,5-dioxocyclopent-3-en-1-ylidene)pentyl acetate (4l): R_f = 0.67 ($CHCl_3$); colorless oil; IR ($CHCl_3$) *v* 1767, 1674 (C=O), 1651 (>C=C<); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.42 (2H, sept, *J* = 6.1 Hz, >CH-O ×2), 2.84 (2H, t, *J* = 7.3 Hz, CH_2), 2.31 (3H, s, $COCH_3$), 1.59-1.49 (2H, m, CH_2), 1.42-1.20 (4H, m, CH_2 ×2), 1.35 (6H, d, *J* = 6.1 Hz, CH_3 ×2), 1.33 (6H, d, *J* = 6.1 Hz, CH_3 ×2), 0.92 (3H, t, *J* = 7.3 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ185.7, 184.2 (C-1, C-3), 168.0 ($\underline{C}OCH_3$), 161.2 (>C=), 149.6, 149.4 (C-4, C-5), 115.9 (C-2), 74.9, 74.7 (>CH-O), 31.6, 28.4 (-CH_2-), 23.1 (2C), 23.0 (2C) (CH_3), 22.5 (CH_2), 21.0 ($CO\underline{C}H_3$), 13.8 (CH_3); MS *m/z* (rel intensity) 339 (M^++H, 6), 297 (52), 255 (24), 213 (100); FAB HRMS (acetone/NBA): calcd for $C_{18}H_{27}O_6$ (M+H) 339.1808; Found 339.1809.

Reaction of Squarates 1i-l Having a C–C Unsaturated Group with Alkenes. To an alkenyl or alkynyl-substituted squarate **1** (0.5 mmol) and an alkene (0.5 mmol) in AcOH (10 mL), $Mn(OAc)_3$ (1 mmol) was added and the mixture was stirred at room temperature, 80 °C, or heated under reflux (see in Table 3). After the work-up mentioned above, the following products **8**, **9**, and **10** were obtained in the yields shown in Table 3.



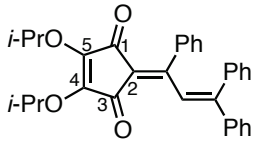
8i



crystal structure of **8i**

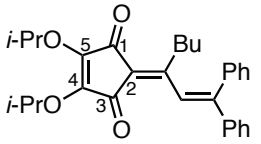
2-(3,3-Diphenylallyl)-4,5-diisopropoxycyclopent-4-ene-1,3-dione (8i): R_f = 0.76 (Et_2O/hexane 7:3 v/v); yellow plates; mp 75 °C; IR ($CHCl_3$) *v* 1685 (C=O), 1608 (>C=C<); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39-7.15 (10H, m, arom H), 5.98 (1H, t, *J* = 7.4 Hz, =CH-), 5.44 (2H, sept, *J* = 6.1 Hz, >CH-O ×2), 2.82 (1H, t, *J* = 5.7 Hz, >CH-), 2.62 (2H, dd, *J* = 7.4, 5.7 Hz, CH_2), 1.33 (6H, d, *J* = 6.1 Hz, CH_3 ×2), 1.31 (6H, d, *J* = 6.06 Hz, CH_3 ×2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.1 (2C) (C-1, C-3), 151.0 (2C) (C-4, C-5), 144.5, 142.5 (arom C), 139.6 (>C=), 130.1 (2C), 128.4 (2C), 128.2 (2C), 127.5 (2C), 127.39, 127.36 (arom CH), 123.6 (-C=), 74.5 (2C) (>CH-O), 49.4 (C-2), 27.4 (CH_2), 22.94 (2C), 22.92 (2C) (CH_3); MS *m/z* (rel intensity) 405 (M^++H, 36), 321 (30), 193 (100), 183 (46), 115 (18); FAB HRMS (acetone/NBA):

calcd for $C_{26}H_{29}O_4$ (M+H) 405.2066; Found 405.2078. X-Ray crystallographic data: empirical formula $C_{26}H_{28}O_4$; formula weight 404.50; yellow plates; crystal dimensions 0.40 x 0.30 x 0.50 mm; triclinic; space group P$\bar{1}$ (no.#2); a = 9.3514(7), b = 9.8113(7), c = 12.991(1) Å, α = 71.520(4), β = 79.687(4), γ = 81.862(4)°, V = 1107.6(1) Å^3, Z = 2; D_{calcd} = 1.213 g/cm^3; F(000) = 432.00; μ(MoKα) = 0.81 cm^{-1}; $2\theta_{max}$ = 55.0°; No. of reflections measured, total: 9283, unique: 4868; No. of observations (I>3.00σ(I), 2θ<54.95°) 3439; No. of variables 271; Reflection/parameter ratio was 12.69; R = 0.047; R_w = 0.074; GOF = 1.20. X-Ray coordinates were deposited with the Cambridge Crystallographic Data Centre: **8i**: CCDC 1870577.



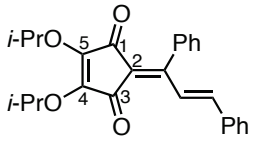
8k

4,5-Diisopropoxy-2-(1,3,3-triphenylallylidene)cyclopent-4-ene-1,3-dione (8k): R_f = 0.48 ($CHCl_3$); orange oil; IR ($CHCl_3$) ν 1666 (C=O), 1612 (>C=C<); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (1H, s, -CH=), 7.31-7.28 (5H, m, arom H), 7.02-6.92 (8H, m, arom H), 6.81-6.78 (2H, m, arom H), 5.47 (1H, sept, J = 6.1 Hz, >CH-O), 5.39 (1H, sept, J = 6.1 Hz, >CH-O), 1.36 (6H, d, J = 6.1 Hz, CH_3 ×2), 1.27 (6H, d, J = 6.1 Hz, CH_3 ×2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 187.9, 185.4 (C-1, C-3), 153.6, 151.2 (>C=), 149.9, 149.5 (C-4, C-5), 142.2, 139.8, 137.1 (arom C), 130.6 (2C), 130.5 (2C) (arom CH), 129.0 (-CH=), 128.8, 128.6 (2C), 128.4 (3C), 127.6 (2C), 127.4, 126.7 (2C) (arom CH), 123.4 (C-2), 74.6, 74.4 (>CH-O), 23.1 (2C) (CH_3), 23.0 (2C) (CH_3); MS *m/z* (rel intensity) 479 (M^++H, 100), 437 (24), 365 (22), 267 (24), 154 (32); FAB HRMS (acetone/NBA): calcd for $C_{32}H_{31}O_4$ (M+H) 479.2222; Found 479.2222.



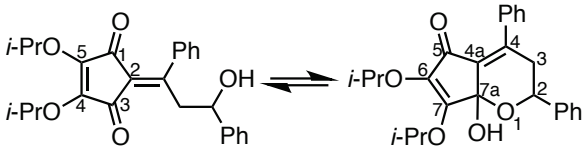
8l

2-(1,1-Diphenylhept-1-en-3-ylidene)-4,5-diisopropoxycyclopent-4-ene-1,3-dione (8l): R_f = 0.71 ($CHCl_3$); yellow oil; IR ($CHCl_3$) ν 1665 (C=O), 1618 (>C=C<); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (1H, s, -CH=), 7.33-7.30 (8H, m, arom H), 7.19-7.15 (2H, m, arom H), 5.46 (1H, sept, J = 6.1 Hz, >CH-O), 5.38 (1H, sept, J = 6.1 Hz, >CH-O), 2.45 (2H, t, J = 7.2 Hz, CH_2), 1.37-1.26 (2H, m, CH_2), 1.35 (6H, d, J = 6.1 Hz, CH_3 ×2), 1.33 (6H, d, J = 6.1 Hz, CH_3 ×2), 1.11 (2H, sext, J = 7.2 Hz, CH_2), 0.74 (3H, t, J = 7.2 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 188.4, 187.7 (C-1, C-3), 158.3 (>C=), 150.0, 149.0 (C-4, C-5), 142.8, 140.4 (arom C), 130.4 (2C) (arom CH), 130.3 (>C=), 128.8 (2C), 128.5, 128.4, 128.38 (4C) (arom CH), 128.0 (-CH=), 123.6 (C-2), 74.5, 74.4 (>CH-O), 32.9, 30.7 (CH_2), 23.1 (2C), 23.0 (2C) (CH_3), 22.8 (CH_2), 13.8 (CH_3); MS *m/z* (rel intensity) 459 (M^++H, 14), 317 (80), 281 (12), 207 (18), 147 (34), 73 (100); FAB HRMS (acetone/NBA): calcd for $C_{30}H_{35}O_4$ (M+H) 459.2535; Found 459.2534.



9k

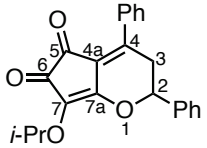
(*E*)-2-(1,3-Diphenylallylidene)-4,5-diisopropoxycyclopent-4-ene-1,3-dione (9k): R_f = 0.50 ($CHCl_3$); yellow oil; IR ($CHCl_3$) ν 1666 (C=O), 1612 (>C=C<); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.85 (1H, d, J = 16.0 Hz, -CH=), 7.49-7.42 (4H, m, arom H), 7.32-7.25 (4H, m, arom H), 7.19-7.16 (2H, m, arom H), 6.52 (1H, d, J = 16.0 Hz, -CH=), 5.47 (1H, sept, J = 6.1 Hz, >CH-O), 5.44 (1H, sept, >CH-O), 1.39 (6H, d, J = 6.1 Hz, CH_3 ×2), 1.27 (6H, d, J = 6.1 Hz, CH_3 ×2); MS *m/z* (rel intensity) 403 (M^++H, 100), 391 (54), 369 (30), 361 (42), 319 (44); FAB HRMS (acetone/NBA): calcd for $C_{26}H_{27}O_4$ (M+H) 403.1909; Found 403.1911.



10k

An equilibrium mixture of 2-(3-hydroxy-1,3-diphenylpropylidene)-4,5-diisopropoxycyclopent-4-ene-1,3-dione and 7a-hydroxy-6,7-diisopropoxy-2,4-diphenyl-3,7a-dihydrocyclopenta[*b*]pyran-5(2*H*)-one (10k): R_f = 0.23 ($CHCl_3$); orange microcrystals; mp 93-95, 137-139 °C; IR ($CHCl_3$) ν 3468 (OH), 1666 (C=O), 1628 (>C=C<); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41-7.27 (10H, m, arom H), 5.49 (1H, sept, J = 6.1 Hz, >CH-O), 5.42 (1H, sept, J = 6.1 Hz, >CH-O), 4.63 (1H, dd, J = 10.5, 3.1 Hz, O–C*H*-2), 3.96 (1H, dd, J = 12.7, 10.5 Hz, *H*CH-3), 3.16, 3.14 (1H, br, OH, disappeared by D_2O exchange experiment), 3.01 (1H, dd, J = 12.7, 3.1 Hz, HC*H*-3), 1.40 (3H, d, J = 6.1 Hz, CH_3), 1.38 (3H, d, J = 6.1 Hz, CH_3), 1.29 (3H, d, J = 6.1 Hz, CH_3), 1.28 (3H, d, J = 6.1 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.5, 185.1, 155.4, 150.4, 148.9, 144.8, 139.0, 129.2, 128.6 (2C), 128.3 (2C), 128.0 (2C), 127.7, 125.8 (2C), 125.6, 74.9, 74.8, 73.3, 45.3, 23.1, 23.06, 23.02, 23.0.

When the equilibrium mixture **10k** was recrystallized from acetone/water at reflux temperature, the hydroxypyranone was converted into the diketone **11k** (60% yield) via de-isopropanol.



11k

7-Isopropoxy-2,4-diphenyl-2,3-dihydrocyclopenta[*b*]pyran-5,6-dione (11k): Yield 60%; R_f = 0.42 ($CHCl_3$); orange microcystals; mp 153-154 °C; IR ($CHCl_3$) ν 1695 (C=O), 1562 (>C=C<); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55-7.52 (2H, m, arom H), 7.47-7.45 (5H, m, arom H), 7.41-7.39 (3H, m, arom H), 5.41 (1H, dd, J = 9.7, 3.9 Hz, O–CH_{ax}-2), 5.37 (1H, sept, J = 6.1 Hz, >CH-O), 3.19 (1H, dd, J = 17.8, 9.7 Hz,

C$\underline{H}_{ax}$-3), 3.07 (1H, dd, J = 17.8, 3.9 Hz, C$\underline{H}_{eq}$-3), 1.34 (3H, d, J = 6.1 Hz, CH_3), 1.32 (3H, d, J = 6.1 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.3, 178.8 (C-5, C-6), 168.4 (C-7), 140.2 (C-7a), 138.0 (arom C), 135.7 (C-4), 135.0 (arom C), 130.1, 129.4, 129.2 (2C), 128.6 (2C), 128.4 (2C), 126.5 (2C) (arom CH), 119.4 (C-4a), 79.8 (C-2), 73.9 (>CH-O), 37.3 (C-3), 22.94, 22.92 (CH_3); MS *m/z* (rel intensity) 361 (M^++H, 100), 318 (44), 215 (12), 154 (16), 91 (14); FAB HRMS (acetone/NBA): calcd for $C_{23}H_{21}O_4$ (M+H) 361.1440; Found 361.1447.

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REFERENCES AND NOTES

1. a) H.-E. Sprenger and W. Ziegenbein, *Angew. Chem., Int. Ed. Engl.*, 1968, **7**, 530; b) R. West, H. Y. Niu, D. L. Powell, and M. V. Evans, *J. Am. Chem. Soc*., 1960, **82**, 6204; c) R. West and D. L. Powell, *J. Am. Chem. Soc.*, 1963, **85**, 2577; d) M. Ito and R. West, *J. Am. Chem. Soc*., 1963, **85**, 2580; e) R. West, H. Y. Niu, and M. Ito, *J. Am. Chem. Soc*., 1963, **85**, 2584.
2. a) H. Y. Zang, H. N. Miras, J. Yan, D.-L. Long, and L. Cronin, *J. Am. Chem. Soc.*, 2012, **134**, 11376; b) Y.-S. Liu, M.-F. Tang, and K.-H. Lii, *Dalton Trans*., 2009, 9781; c) C.-M. Wang and K.-H. Lii, *Inorg. Chem*., 2009, **48**, 6335; d) Z. Hulvey and A. K. Cheetham, *Solid State Sci*., 2007, **9**, 137; e) O. Z. Yesilel, H. Pasaoglu, G. Kastas, H. Ölmez, and O. Büyükgüngör, *Z. Naturforsch.*, 2006, **61b**, 1249.
3. a) H. W. Moore and O. H. W. Decker, *Chem. Rev*., 1986, **86**, 821; b) M. Ohno, Y. Yamamoto, and S. Eguchi, *Synlett*, 1998, 1167; c) L. A. Paquette, *Eur. J. Org. Chem.*, 1998, 1709; d) L. S. Liebeskind, *Tetrahedron*, 1989, **45**, 3053; e) S. Niwayama, E. A. Kallel, C. Sheu, and K. N. Houk, *J. Org. Chem*., 1996, **61**, 2517; f) C. S. Tomooka, H. Liu, and H. W. Moore, *J. Org. Chem.*, 1996, **61**, 6009; g) L. Sun and L. S. Liebeskind, *J. Am. Chem. Soc*., 1996, **118**, 12473.
4. K.-Y. Law, *Chem. Rev*., 1993, **93**, 449.
5. a) J. L. Kraus, *Tetrahedron Lett*., 1985, **26**, 1867; b) M. W. Reed and H. W. Moore, *J. Org. Chem.*, 1987, **52**, 3491; c) E. F. Campbell, A. K. Park, W. A. Kinney, R. W. Fengl, and L. S. Liebeskind, *J. Org. Chem*., 1995, **60**, 1470; d) T. Shinada, T. Ishida, and Y. Ohfune, *J. Synth. Org. Chem. Jpn*., 2007, **65**, 30.
6. a) L. A. Paquette, T. M. Morwick, and J. T. Negri, *Tetrahedron*, 1996, **52**, 3075, b) L. A. Paquette and F. Geng, *J. Am. Chem. Soc*., 2002, **124**, 9199; c) J. M. MacDougall, V. J. Santora, S. K. Verma,

P. Turnbull, C. R. Hernandez, and H. W. Moore, *J. Org. Chem.*, 1998, **63**, 6905; d) M. W. Reed and H. W. Moore, *J. Org. Chem*., 1988, **53**, 4166.

7. a) R. Matsumoto and H. Nishino, *Synth. Commun*., 2015, **45**, 1807; b) S. Tadano, Y. Mukaeda, and H. Ishikawa, *Angew. Chem. Int. Ed*., 2013, **52**, 7990; c) S. Tadano, Y. Sugimachi, M. Sumimoto, S. Tsukamoto, and H. Ishikawa, *Chem. Eur. J*., 2016, **22**, 1277.
8. a) S. Cohen, J. R. Lacher, and J. D. Park, *J. Am. Chem. Soc*., 1959, **81**, 3480; b) I. Shimizu, *J. Synth. Org. Chem. Jpn*.,1995, **53**, 330.
9. a) L. S. Liebeskind, R. W. Fengl, K. R. Wirtz, and T. T. Shawe, *J. Org. Chem.*, 1988, **53**, 2482; b) E. V. Dehmlow and H. G. Schell, *Chem. Ber*., 1980, **113**, 1.
10. a) L. S. Liebeskind and A. Bombrum, *J. Org. Chem*., 1994, **59**, 1149; b) L. A. Paquette, C. F. Sturino, and P. Doussot, *J. Am. Chem. Soc*., 1996, **118**, 9456; c) Y. Rubin, S. S. Lin, C. B. Knobler, J. Anthony, A. M. Boldi, and F. Diederich, *J. Am. Chem. Soc*., 1991, **113**, 6943.
11. a) Y. Yamamoto, M. Ohno, and S. Eguchi, *J. Am. Chem. Soc*., 1995, **117**, 9653; b) Y. Yamamoto, M. Ohno, and S. Eguchi, *J. Org. Chem.*, 1994, **59**, 4707; c) M. Ohno, I. Oguri, and S. Eguchi, *J. Org. Chem*., 1999, **64**, 8995; d) L. S. Liebeskind, R. Chidambaran, D. M. Mitchell, and B. S. Foster, *Pure Appl. Chem.*, 1988, **60**, 27; e) L. S. Liebeskind, D. M. Mitchell, and B. S. Foster, *J. Am. Chem. Soc.*, 1987, **109**, 7908; f) L. S. Liebeskind and R. W. Fengl, *J. Org. Chem.*, 1990, **55**, 5359.
12. a) W. J. de Klein, in *Organic Syntheses by Oxidation with Metal Compounds*, ed. by W. J. Mijis and C. R. H. I. de Jonge, Plenum Press, New York, 1986, pp. 261-314; b) *Radicals in Organic Synthesis*, Vol. 1, ed. by P. Renaud and M. P. Sibi, Wiley-VCH, 2001; c) J. W. Burton, in *Encyclopedia of Radicals in Chemistry, Biology and Materials*, ed. by C. Chatgilialoglu and A. Studer, Wiley, 2012, pp. 901-941; d) I. B. Krylov, A. O. Terent'ev, V. P. Timofeev, B. N. Shelimov, R. A. Novikov, V. M. Merkulova, and G. I. Nikishin, *Adv. Synth. Catal.*, 2014, **356**, 2266; e) G. G. Melikyan, *Org. React*., 1997, **49**, 427.
13. a) K. Kurosawa, *Bull. Chem. Soc. Jpn.*, 1969, **42**, 1456; b) K. Kurosawa and J. Higuchi, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 1132.
14. a) K. Kurosawa, Y. Sasaki, and M. Ikeda, *Bull. Chem. Soc. Jpn.*, 1973, **46**, 1498; b) S. Ueda and K. Kurosawa, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 193.
15. K. Nogami and K. Kurosawa, *Bull. Chem. Soc. Jpn.*, 1974, **47**, 505.
16. K. Kurosawa and F. Araki, *Bull. Chem. Soc. Jpn.*, 1979, **52**, 529.
17. a) M. S. South and L. S. Liebeskind, *J. Org. Chem.*, 1982, **47**, 3815; b) O. Abou-Teim, M. C. Goodland, and J. F. W. McOmie, *J. Chem. Soc., Perkin Trans. 1*, 1983, 2659.
18. L. S. Liebeskind, S. Iyer, and C. F. Jewell, Jr., *J. Org. Chem.*, 1986, **51**, 3065.

19. a) A. M. Creighton and L. M. Jackman, *J. Chem. Soc.*, 1960, 3138; b) R. M. Elofson, L. A. Baker, F. F. Gadallah, and R. A. Sikstrom, *J. Org. Chem*., 1964, **29**, 1355; c) M. V. Bhatt, K. M. Kamath, and M. Ravindranathan, *J. Chem. Soc. C*, 1971, 3344; d) K. Praefcke and H. Simon, *Chem. Ber*., 1976, **109**, 3915; e) Y. Tsujimoto, Y. Shigemitsu, T. Miyamoto, and Y. Odaira, *Bull. Chem. Soc. Jpn*., 1976, **49**, 1445; f) M. Pfau, F. Gobert, J.-C. Gramain, and M.-F. Lhomme, *J. Chem. Soc., Perkin Trans. 1*, 1978, 509; g) P. B. Jones, M. P. Pollastri, and N. A. Porter, *J. Org. Chem*., 1996, **61**, 9455; h) M. Takahashi, T. Fujita, S. Watanabe, and M. Sakamoto, *J. Chem. Soc., Perkin Trans. 2*, 1998, 487; i) J. Pika, A. Konosonoks, R. M. Robinson, P. N. D. Singh, and A. D. Gudmundsdottir, *J. Org. Chem*., 2003, **68**, 1964.
20. a) J. B. Vincent, H.-R. Chang, K. Foiling, J. C. Huffman, G. Christou, and D. N. Hendrickson, *J. Am. Chem. Soc*., 1987, **109**, 5703; b) J. B. Vincent, C. Christmas, J. C. Huffman, G. Christou, H.-R. Chang, and D. N. Hendrickson, *J. Chem. Soc., Chem. Commun*., 1987, 236; c) C. Christmas, J. B. Vincent, J. C. Huffman, G. Christou, H.-R. Chang, and D. N. Hendrickson, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 915; d) W. E. Fristad and J. R. Peterson, *J. Org. Chem*., 1985, **50**, 10; e) W. E. Fristad, J. R. Peterson, A. B. Ernst, and G. B. Urbi, *Tetrahedron*, 1986, **42**, 3429; f) B. B. Snider, *Tetrahedron*, 2009, **65**, 10738.
21. B. B. Snider, *Chem. Rev*., 1996, **96**, 339.
22. M. W. Reed, D. J. Pollart, S. T. Perri, L. D. Foland, and H. W. Moore, *J. Org. Chem.*, 1988, **53**, 2477.
23. N. Fujimoto, H. Nishino, and K. Kurosawa, *Bull. Chem. Soc. Jpn*., 1986, **59**, 3161.
24. S. Cohen and S. G. Cohen, *J. Am. Chem. Soc*., 1966, **88**, 1533.
25. E. Peña-Cabrera and L. S. Liebeskind, *J. Org. Chem.*, 2002, **67**, 1689.
26. H. Nishino, S. Tategami, T. Yamada, J. D. Korp, and K. Kurosawa, *Bull. Chem. Soc. Jpn*., 1991, **64**, 1800.
27. N. Kikue, T. Takahashi, and H. Nishino, *Heterocycles*, 2015, **90**, 540.
28. K. Yamaguchi and D. T. Sawyer, *Inorg. Chem*., 1985, **24**, 971.
29. a) V. Kalyani, H. Manohar, and N. V. Mani, *Acta Cryst.*, 1967, **23**, 272; b) V. Kalyani and M. Vijayan, *Curr. Sci*., 1967, **36**, 662.
30. H. Yin, S. W. Dantale, N. G. Akhmedov, and B. C. G. Söderberg, *Tetrahedron*, 2013, **69**, 9284; Erratum: *Tetrahedron*, 2013, **69**, 10516.
31. a) P. Turnbull, M. J. Heileman, and H. W. Moore, *J. Org. Chem*., 1996, **61**, 2584; b) T. Shinada, Y. Ooyama, K. Hayashi, and Y. Ohfune, *Tetrahedron Lett*., 2002, **43**, 6755.