Pergamon

SCIENCE DIRECT®

Tetrahedron 59 (2003) 755–765

TETRAHEDRON

Synthesis of polyfunctionalized furans from 3-acetyl-1-aryl-2-pentene-1,4-diones

Satoaki Onitsuka and Hiroshi Nishino*

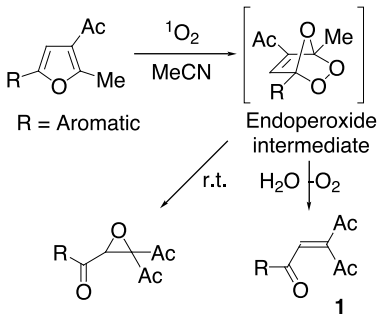
Department of Chemistry, Faculty of Science, Kumamoto University, Kurokami 2-39-1, Kumamoto 860-8555, Japan

Received 18 November 2002; revised 11 December 2002; accepted 11 December 2002

Abstract—The BF_3-catalyzed cyclization of 3-acetyl-1-aryl-2-pentene-1,4-diones **1a**–**e** in the presence of water in boiling tetrahydrofuran gave bis(3-acetyl-5-aryl-2-furyl)methanes **2a**–**e** in 26–79% yields along with a small amount of 3-acetyl-5-aryl-2-methylfurans **3a**–**e**. The exact structure of **2a** was determined by X-ray crystallography. The use of a half volume of the solvent for the reaction of **1a** resulted in the formation of 2,4-bis(3-acetyl-5-phenyl-2-furfuryl)-3-acetyl-5-phenylfuran (**4**) together with **2a** and **3a**. A similar reaction of **1a** was carried out in the presence of 3-acetyl-5-(4-methylphenyl)-2-methylfuran (**3d**) to afford 4-(3-acetyl-5-phenyl-2-furfuryl)-3-acetyl-5-(4-methylphenyl)-2-methylfuran (**5**) in 49% yield. The BF_3-catalyzed reaction of **1a** with 2,4-pentanedione in dry tetrahydrofuran at 23°C gave 3-(3-acetyl-5-phenyl-2-furfuryl)-4-hydroxy-3-penten-2-one (**6a**) and 3-(3-acetyl-2-methyl-4-phenyl-5-furyl)-4-hydroxy-3-penten-2-one (**7a**) in 66 and 24% yields, respectively. The product distribution depended on the reaction temperature. A similar reaction of **1b**–**e** also yielded the corresponding trisubstituted furans **6b**–**e** and tetrasubstituted furans **7b**–**e** in good yields. These results suggested the presence of the furfuryl carbocation intermediate **A** during the reaction. The one-pot synthesis of **6a** and **7a** was also achieved by a similar reaction using phenylglyoxal. The deoxygenation of **1a** with triphenylphosphine gave **3a** in 88% yield, while **1a** was treated with concentrated hydrochloric acid to yield 3-acetyl-2-chloromethyl-5-phenylfuran (**8**) which was quantitatively transformed in ethanol into 3-acetyl-2-ethoxymethyl-5-phenylfuran (**9**) and in water into 3-acetyl-5-phenylfurfuryl alcohol (**10**), respectively. In addition, the Diels–Alder reaction of cyclopantadiene with **1a** gave the corresponding [4+2] cycloaddition products **11** and **12**.

1. Introduction

Furans and their derivatives are widely present in nature[1] and not only one of the most important heterocyclic compounds in organic chemistry,[2] but also building blocks which are essential for the total synthesis of the complicated naturally occurring metabolites.[3] Furthermore, polyfunctionalized furans are versatile and convenient synthetic starting materials for the preparation of a variety of heterocyclic and acyclic compounds.[4] In connection with our study of the synthesis and reaction of substituted furan derivatives,[5] we recently found that endoperoxide intermediates[6] obtained by the photosensitized oxygenation of furans[7] were selectively transformed into pentenediones **1** and oxiranes depending on the reaction conditions (Scheme 1).[8] As the pentenediones **1** were not very stable in air due to the extremely electron-deficient alkene, it prompted us to explore the reactivity of the pentenediones **1**.[9] Since the acid-catalyzed cyclization of 1,4-diketones is well-known,[4c,10] we first examined the BF_3-catalyzed cyclization of the pentenediones **1**.[11] Surprisingly, the pentenediones **1** were converted into very stable crystalline bis(furyl)-methane derivatives. Furthermore, the presence of a strong nucleophile in a similar reaction led to the formation of polyfunctionalized furans. Although the synthesis of furans has been well-documented over the past three decades[2,4,12] and a very new methodology for the facile synthesis of substituted furans by palladium-catalyzed reaction was also reported,[13] we scrutinized the typical BF_3-catalyzed reaction of the pentenediones **1** from the standpoint of the synthesis of the polyfunctionalized furans. In addition, the synthetic applications using the pentenediones **1** were also investigated in order to evaluate their synthetic utility.

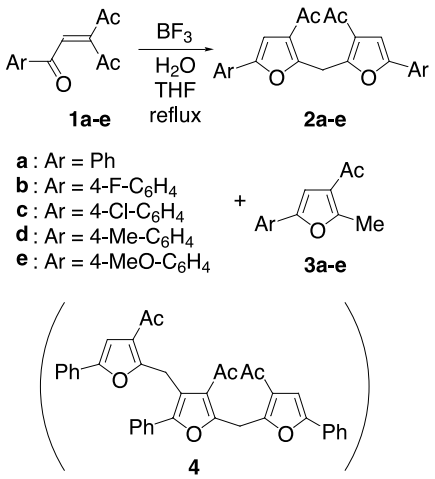


Scheme 1.

Keywords: BF_3-catalyzed cyclization; 3-acetyl-1-aryl-2-pentene-1,4-diones; polyfunctionalized furans; bis(furyl)methanes; trisubstituted furans; tetrasubstituted furans; furfuryl carbocation intermediate; Diels–Alder reaction.

* Corresponding author. Tel./fax: +81-96-342-3374;
e-mail: nishino@aster.sci.kumamoto-u.ac.jp

0040–4020/03/$ - see front matter
PII: S0040-4020(02)01597-1



Scheme 2.

ture of **2a** was characterized by spectroscopic means, elemental analysis, and finally X-ray crystallography, and found to be bis(3-acetyl-5-phenyl-2-furyl)methane which showed C_2 symmetry at the methylene group (Fig. 1). The treatment of the pentenediones **1b–e** with $BF_3{\cdot}Et_2O$ under the same reaction conditions preferentially gave the corresponding bis(furyl)methanes **2b–e** together with a small amount of the trisubstituted furans **3b–e** (entries 6–9).

In order to scrutinize the reaction, the reaction of **1a** was carried out in a half volume of the solvent, thus leading to the decrease of the yield of **2a** and the new production of the trimeric furan derivative **4** which was determined to be 2,4-bis(3-acetyl-5-phenyl-2-furfuryl)-3-acetyl-5-phenylfuran based on the spectroscopic data (FAB MS *m/z* 583, M+1) and elemental analysis (entry 4). On the other hand, a similar reaction under dilute conditions resulted in the increased yield of **3a** (entry 5). Since the trimeric furan **4** seemed to be formed by the reaction of **2a** with the corresponding furfuryl carbocation intermediate, we examined the BF_3-catalyzed reaction of **1a** in the presence of an electron-rich furan derivative such as

Table 1. BF_3-Catalyzed cyclization of 3-acetyl-1-aryl-2-pentene-1,4-diones **1a–e**

Entry	Substrate	Water (equiv.)	Conc.[a] (mol/dm^3)	Time (h)	Product (yield, %)[b]		
1	**1a**: Ar=Ph	0	0.2	0.5	**2a** (21)		
2	**1a**: Ar=Ph	5	0.2	0.5	**2a** (62)		
3	**1a**: Ar=Ph	10	0.1	1.5	**2a** (79)	**3a** (4)	
4	**1a**: Ar=Ph	10	0.2	1	**2a** (62)	**3a** (3)	**4** (15)
5	**1a**: Ar=Ph	10	0.04	6	**2a** (61)	**3a** (13)	
6	**1b**: Ar=4-F-C_6H_4	10	0.1	2	**2b** (67)	**3b** (6)	
7	**1c**: Ar=4-Cl-C_6H_4	10	0.1	2	**2c** (63)	**3c** (3)	
8	**1d**: Ar=4-Me-C_6H_4	10	0.1	2	**2d** (65)	**3d** (5)	
9	**1e**: Ar=4-MeO-C_6H_4	10	0.1	2	**2e** (26)	**3e** (10)	

The reaction of the pentenedione **1** (0.5 mmol) with $BF_3{\cdot}Et_2O$ (5.0 mmol) was carried out in tetrahydrofuran (0.5–12.5 mL) containing water (5.0 mmol except for entries 1 and 2) at the reflux temperature.
[a] The concentration of **1** in tetrahydrofuran.
[b] Isolated yield based on the amount of pentenedione **1** used.

2. Results and discussion

2.1. BF_3-Catalyzed cyclization of 3-acetyl-1-aryl-2-pentene-1,4-diones 1a–e

In order to prepare a practical amount of 3-acetyl-1-phenyl-2-pentene-1,4-dione (**1a**), we developed the synthesis of **1a** using phenylglyoxal and 2,4-pentanedione.[9] The Lewis acid-catalyzed crossed Aldol condensation in tetrahydrofuran afforded **1a** in low yield.[14] The Knoevenagel condensation using pyridine in boiling tetrahydrofuran gave **1a** in 87% yield.[9,15] Finally we obtained **1a** in quantitative yield (98%) by the reaction in boiling acetonitrile for 12 h in the absence of catalyst. Since we had enough **1a** on hand, we examined the BF_3-catalyzed cyclization of **1a**.

The pentenedione **1a** was allowed to react with $BF_3{\cdot}Et_2O$ in boiling tetrahydrofuran. Although the reaction was complicated, we managed to isolate the dimeric furan **2a** (Scheme 2 and Table 1, entry 1). We postulated that some nucleophilic reagents such as water were necessary to control the reaction. As expected, the addition of water led to the increased yield of **2a** (entry 2). When 10 equiv. of water based on **1a** was added to the mixture, the maximum yield of **2a** (79%) was achieved along with a small amount of 3-acetyl-2-methyl-5-phenylfuran (**3a**) (entry 3). The struc-

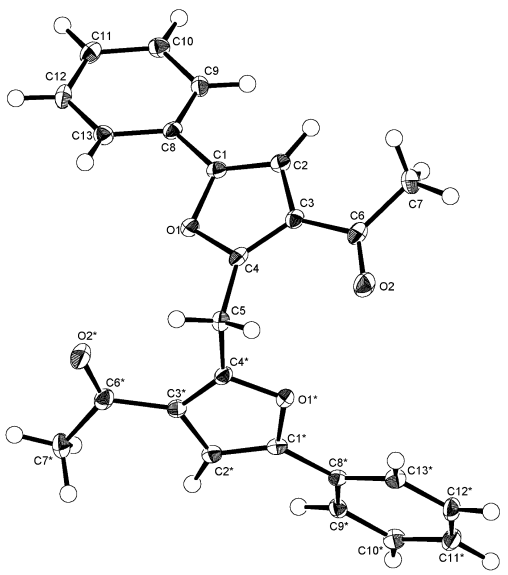
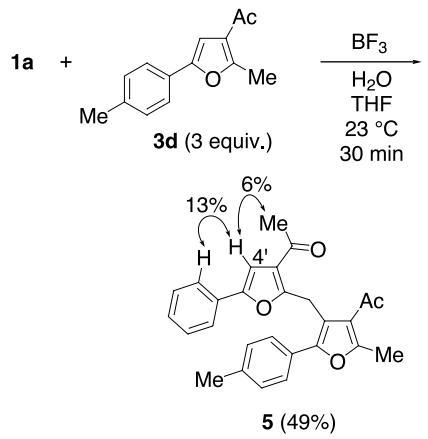
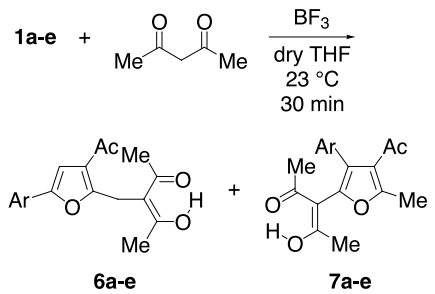


Figure 1. ORTEP diagram of bis(furyl)methane **2a**.



Scheme 3.



Scheme 4.

Table 2. BF_3-Catalyzed reaction of 3-acetyl-1-aryl-2-pentene-1,4-diones **1a–e** with 2,4-pentanedione

Entry	Substrate	Temperature (°C)	Time (h)	Product (yield, %)[a]	
1	**1a**: Ar=Ph	0	2	**6a** (34)	**7a** (52)
2	**1a**: Ar=Ph	23	0.5	**6a** (66)	**7a** (24)
3	**1a**: Ar=Ph	Reflux	0.5	**6a** (77)	**7a** (16)
4	**1b**: Ar=4-F-C_6H_4	23	0.5	**6b** (53)	**7b** (23)
5	**1c**: Ar=4-Cl-C_6H_4	23	0.5	**6c** (76)	**7c** (8)
6	**1d**: Ar=4-Me-C_6H_4	23	0.5	**6d** (34)	**7d** (53)
7	**1e**: Ar=4-MeO-C_6H_4	23	0.5	**6e** (15)	**7e** (59)

The reaction was carried out in dry tetrahydrofuran (5 mL) at the molar ratio of **1** (1.0 mmol)/2,4-pentanedione/BF_3·Et_2O=1:10:10.
[a] Isolated yield based on the amount of pentenedione **1** used.

3-acetyl-5-(4-methylphenyl)-2-methylfuran (**3d**)[5c,8] to trap the furfuryl carbocation intermediate. The pentenedione **1a** was allowed to react with 3 equiv. of **3d** in the presence of BF_3·Et_2O in tetrahydrofuran containing water at 23°C for 30 min, giving a dimeric furan **5** in 49% yield (Scheme 3). The irradiation of the H-4′ proton in the ^{1}H NMR spectrum of **5** showed an enhancement of the *ortho* phenyl proton (δ 7.46–7.43) and the acetyl proton (δ 2.56) signals. Therefore, the structure of **5** was determined to be 4-(3-acetyl-5-phenyl-2-furfuryl)-3-acetyl-5-(4-methyl-phenyl)-2-methylfuran. Since we obtained evidence for the presence of the furfuryl carbocation intermediate in the BF_3-catalyzed cyclization of the pentenediones, we next investigated the reaction using more reactive nucleophiles such as the 2,4-pentanedionate ion.

2.2. BF_3-Catalyzed reaction of pentenediones 1a–e with 2,4-pentanedione[9]

A mixture of **1a** and 2,4-pentanedione (10 equiv.) was allowed to react with BF_3·Et_2O (10 equiv.) in dry tetrahydrofuran at 23°C. It was a mild exothermic reaction, and the trisubstituted furan **6a** and tetrasubstituted furan **7a** were obtained in 66 and 24% yields, respectively (Scheme 4 and Table 2, entry 2). Since the mass spectra of **6a** and **7a** showed the same molecular ion peak (*m*/*z* 298), both products were isomers of each other. The ^{1}H NMR spectra of **6a** and **7a** revealed a broad singlet at δ 16.88 and 16.75, respectively, which were assigned to the intramolecular hydrogen-bonded hydroxyl proton. The IR spectra also showed weak intramolecular hydrogen-bonded hydroxyl broad absorptions at 3700–3200 cm^{-1}, and the enolizable β-diketocarbonyl absorptions appeared at 1673–1678 and 1610–1600 cm^{-1}. These spectroscopic data indicated the presence of the 4-hydroxy-3-penten-2-one moiety. The ^{1}H and ^{13}C NMR spectra of **6a** were similar to those of **3a** except for the (4-hydroxy-2-oxo-3-penten-3-yl)methyl group in place of the methyl group at the C-2′ carbon. Therefore, it was easy to characterize the structure of **6a** which was the 3-(3-acetyl-5-phenyl-2-furfuryl)-4-hydroxy-3-penten-2-one. Since the furan **7a** was substituted by four different functional groups, several regioisomers of **7a** were postulated. However, it was difficult to deduce the structure of **7a** based on the spectroscopic method.[16] The exact structure of **7a** was eventually determined by an X-ray single crystal analysis as 3-(3-acetyl-2-methyl-4-phenyl-5-furyl)-4-hydroxy-3-penten-2-one (Fig. 2). It was found that both the 4-hydroxy-3-penten-2-one moiety and the phenyl

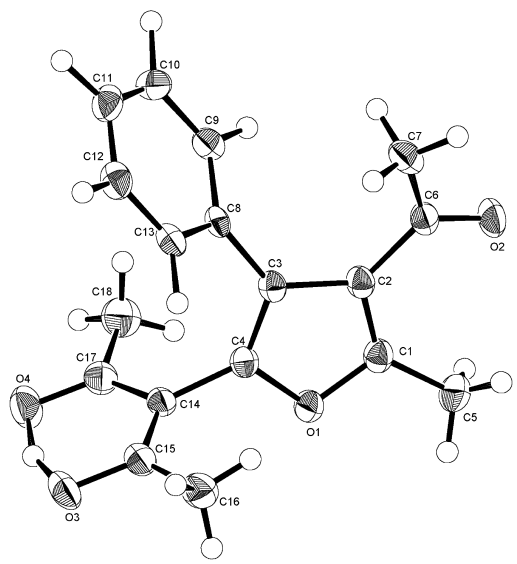


Figure 2. ORTEP drawing of tetrasubstituted furan **7a**.

substituent were not on the same plane of the furan ring in the solid state because of the steric repulsion of each other.

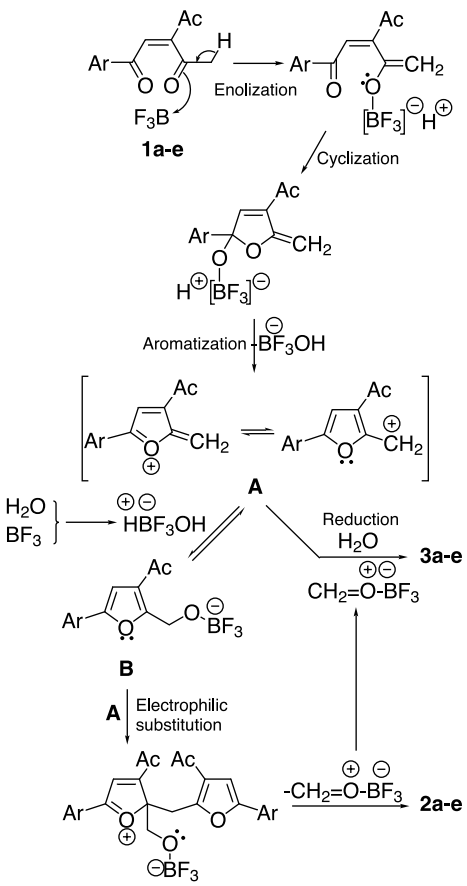
When a similar reaction of **1a** with 2,4-pentanedione was carried out at 0°C for 2 h, the tetrasubstituted furan **7a** was formed rather than **6a** (entry 1), whereas the reaction at the reflux temperature preferentially gave the trisubstituted furan **6a** (entry 3). The reaction of the pentenediones **1b** and **1c** substituted by an electron-attracting group on the phenyl ring at 23°C preferentially gave the trifunctionalized furans **6b** and **6c**, respectively (entries 4 and 5). On the other hand, the pentenediones **1d** and **1e** having an electron-releasing group on the phenyl substituent were allowed to react under similar reaction conditions, mainly affording the tetrasubstituted furans **7d** and **7e** (entries 6 and 7).

2.3. Mechanistic aspect

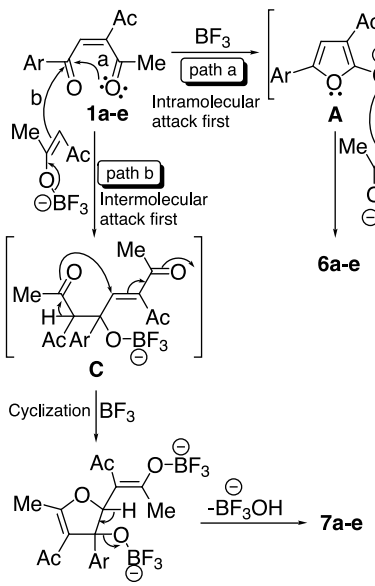
When the reaction of the pentenediones **1a**–**e** was carried out under wet reaction conditions, the BF_3-induced intramolecular cyclization would occur during the first stage of the reaction to give a relatively stable furfuryl carbocation intermediate **A** (Scheme 5). The intermediate **A** might be equilibrated to the corresponding furfuryl alcohol **B** under the wet reaction conditions, which would be attacked by another furfuryl cation **A** at the C-2 position to complete the electrophilic substitution along with releasing formaldehyde, giving the bis(furyl)methanes **2a**–**e**.

It is well-known that the electrophilic substitution of furans is liable to occur 6000 times faster at the α position than at the β one.[17] It was easy to prove the existence of the furfuryl alcohol since the treatment of 3-acetyl-2-chloromethyl-5-phenylfuran (**8**) with water gave the corresponding furfuryl alcohol which was transformed into the corresponding bis(furyl)methane **2a** under the same reaction conditions in the presence of $BF_3{\cdot}Et_2O$ (vide infra). In addition, the presence of the furfuryl carbocation intermediate **A** was also supported by the fact that the trimeric furan **4** would be obtained by the reaction of the furfuryl carbocation intermediate **A** with **2a** formed in situ under the concentration conditions (Table 1, Entry 4) and the dimeric furan **5** would be produced by the reaction of the electron-rich furan **3d** with the furfuryl carbocation intermediate **A**. Although gaseous formaldehyde was not trapped by 2,4-dinitrophenylhydrazine in DMF, it clearly formed formaldehyde since the reduction product **3a** of the corresponding furfuryl carbocation intermediate **A** was formed under the dilute conditions besides **2a** (Table 1, entry 5). The reaction pathway for the formation of the bis(furyl)methanes **2a**–**e** and furans **3a**–**e** is depicted in Scheme 5.

During the reaction with a strong nucleophile such as the 2,4-pentanedione-BF_3 enolate complex under dry conditions, when the electrophilicity of the aroyl carbon in **1b**,**c** would be relatively high because of the presence of electron-withdrawing groups such as the 4-fluoro- and 4-chloro-phenyl groups or the reaction was carried out under reflux temperature, the intramolecular cyclization of the pentendiones **1a**–**e** would preferentially take place to give the thermodynamically stable furfuryl carbocation intermediate **A** (path a in Scheme 6), which would react with the 2,4-pentanedione-BF_3 enolate complex to form trisubstituted furans **6** (Table 2, entries 3–5). While the aroyl carbon would not be sufficiently electrophilic such as **1d**,**e** or the reaction was conducted at 0°C, fast nucleophilic addition of a strong nucleophile such as the 2,4-pentanedione-BF_3 enolate complex to the aroyl carbon should predominantly occur to afford the intermediate **C** (path b in Scheme 6) and subsequent cyclization would give the



Scheme 5.



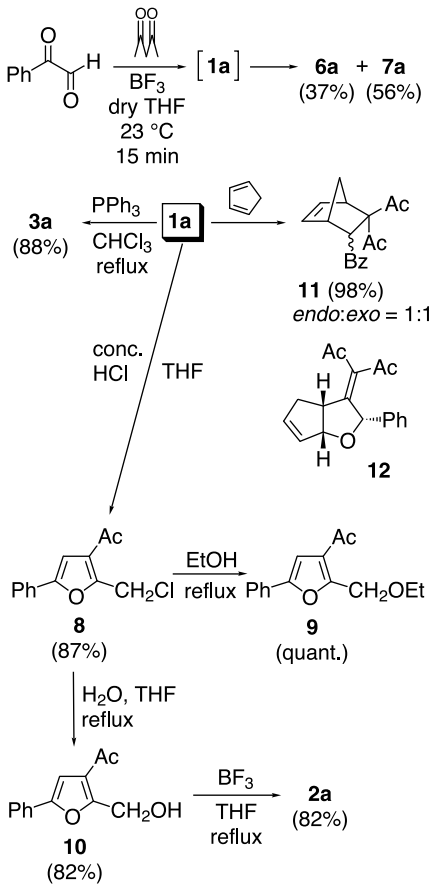
Scheme 6.

tetrasubstituted furans **7** (Table 2, entries 1, 6, 7). The trisubstituted furans **6a**–**e** seem to be thermodynamically controlled and the tetrasubstituted furans **7a**–**e** might just be kinetically controlled reaction products.

2.4. Synthetic applications

Although the BF_3-catalyzed condensation of phenylglyoxal with a stoichiometric amount of 2,4-pentanedione in dry tetrahydrofuran at 23°C gave the pentenedione **1a** in 29% yield, in order to develop the one-pot synthesis of **6a** and **7a**, we examined the reaction using excess amounts of 2,4-pentanedione.[9] As a result, we achieved the one-pot synthesis of **6a** and **7a** using 10 equiv. of 2,4-pentanedione in the BF_3-catalyzed condensation of phenylglyoxal at 23°C for 15 min, giving **6a** and **7a** in 37 and 56% yields, respectively (Scheme 7).

The pentenediones **1a**–**e** are quite unique and extremely electron-deficient alkenes so that they would be useful for organic synthesis. For example, the deoxygenation of **1a** with triphenylphosphine gave **3a** in 88% yield (Scheme 7).[18] The pentenedione **1a** was treated with concentrated hydrochloric acid at 23°C to yield the 3-acetyl-2-chloromethyl-5-phenylfuran (**8**) in 87% yield.[19] The chloromethylfuran **8** was quantitatively transformed into 2-ethoxymethylfuran **9** in boiling ethanol.[19] The hydrolysis of **8** gave the corresponding furfuryl alcohol **10** which was allowed to react with $BF_3{\cdot}Et_2O$ under typical reaction conditions to yield **2a** in 82% yield (Scheme 7).



Scheme 7.

The Diels–Alder reaction of cyclopentadiene with the electron-deficient alkene **1a** deserves comment.[20] In general, *endo* adducts should be predominantly formed during the [4+2] cycloaddition, however, the reaction of the cyclopentadiene with **1a** gave the corresponding *exo* and *endo* adducts **11** together with a unique 2-oxabicyclo[3.3.0]-octene **12** in 96% total yield (**11**-*exo*/**11**-*endo*/**12**=53:12:35) (Scheme 7).[21] The structures of these **11**-*exo*, **11**-*endo*, and **12** products were established by difference NOE experiments. The bicyclic compound **12** might be formed by the intramolecular rearrangement of the *endo* adduct **11**.

3. Conclusion

We revealed that the furfuryl carbocation **A** was an important key intermediate in the synthesis of polyfunctionalized furans using 3-acetyl-1-aryl-2-pentene-1,4-diones **1a**–**e**. In the presence of a weak nucleophile such as water, the BF_3-catalyzed cyclization of **1a**–**e** gave bis-(furyl)methanes **2a**–**e** in good yields along with small amounts of the reduction products **3a**–**e**. On the other hand, a strong nucleophile such as the 2,4-pentanedione-BF_3 enolate complex reacted with the carbocation **A** to give the tri- and tetra-substituted furans **6a**–**e** and **7a**–**e**. Although there are many synthetic methods for furan derivatives, for example, the acid-catalyzed dehydration of 1,4-diketones,[4c] the reduction of 2-butene-1,4-diones with tin(II) chloride,[22] phosphites,[23] zinc powder,[24] or lithium aluminum hydride,[25] and the addition of 2-butene-1,4-diones with acetyl chloride[26] or Grignard reagent,[27] our methodology for the synthesis of polyfunctionalized furan derivatives using the BF_3-catalyzed cyclization of pentenediones **1** is also useful and convenient since many pentenedione derivatives could be prepared from arylglyoxals[9,15b,28] and many kinds of active methylene compounds could be used as strong nucleophiles. In addition, we could also demonstrate the synthetic utility of the pentenediones **1**.

4. Experimental

The melting points are uncorrected. All of the ^1H and ^{13}C NMR spectra were recorded at 300 MHz for ^1H and 75 MHz for ^{13}C, respectively, with tetramethylsilane as the internal standard. The chemical shifts are reported in δ values (ppm). The IR spectra are expressed in cm^{-1}. The elemental analyses were performed at the Analytical Center of Kumamoto University, Kumamoto, Japan, or the Elemental Analysis Center of Kyusyu University, Fukuoka, Japan.

The 3-acetyl-1-aryl-2-pentene-1,4-diones (**1b**–**e**) were prepared according to the literature method.[8] $BF_3{\cdot}Et_2O$, 2,4-pentanedione, and triphenyl phosphine were purchased from Wako Pure Chemical Ind., Ltd, and were used as received. Phenylglyoxal monohydrate was purchased from Tokyo Chemical Industry Co., Ltd, and was used as received.

4.1. Knoevenagel condensation of phenylglyoxal with 2,4-pentanedione

Phenylglyoxal (1.52 g, 10 mmol) and 2,4-pentanedione (1.03 mL, 10 mmol) were dissolved in acetonitrile (5 mL)

and the mixture was heated under reflux for 12 h. The solvent was removed under reduced pressure and the residue was separated by flash column chromatography (Fuji Silysia BW-300 silica gel) with hexane/ethyl acetate (4:1 v/v) as the eluting solvent, thus affording **1a** (2.05 g, 95%) as a pale yellow solid.

4.1.1. 3-Acetyl-1-phenyl-2-pentene-1,4-dione (1a). Pale yellow needles; mp 68.5°C (lit.,[7f] mp 69–71°C); IR ($CHCl_3$) ν 1706, 1666 (C=O), 1597 (C=C–C=O); ^{1}H NMR ($CDCl_3$) δ 8.00–7.40 (5H, m, arom. H), 7.59 (1H, s,=CH–), 2.46 (3H, s, Ac), 2.42 (3H, s, Ac); ^{13}C NMR ($CDCl_3$) δ 202.9, 196.4, 189.9 (C=O), 151.9 (=C<), 136.1 (arom. C), 134.4 (arom. CH), 130.2 (=CH–), 129.0 (2C), 128.7 (2C) (arom. CH), 30.7, 27.2 (Ac). Anal. calcd for $C_{13}H_{12}O_3$: C, 72.21; H, 5.59. Found: C, 72.37; H, 5.59.

4.2. BF_3-Catalyzed cyclization of pentenediones 1a–e

The pentenediones **1a–e** (0.5 mmol) were dissolved in THF (5 mL) containing water (90 μL, 5.0 mmol). $BF_3{\cdot}Et_2O$ (635 μL, 5.0 mmol) was added to the solution and the mixture was heated under reflux for 30 min. The yellow color of the reaction mixture then turned red. Water (20 mL) and a saturated aqueous solution of sodium hydrogencarbonate (30 mL) were added to the reaction mixture, and the aqueous mixture was extracted with chloroform. The extract was washed with water (100 mL) and concentrated to dryness. The residue was separated by flash column chromatography (Fuji Silysia BW-300 silica gel) with chloroform as the eluting solvent, then giving the bis(furyl)methanes **2a–e** and 3-acetyl-5-aryl-2-methylfurans **3a–e**.[5c] The bis(furyl)methanes **2a–e** were further purified by silica gel TLC and recrystallized from methanol or dichloromethane/hexane. The exact structure of the bis(furyl)methane **2a** was determined by X-ray crystallography.

4.2.1. Bis(3-acetyl-5-phenyl-2-furyl)methane (2a). Colorless cubes (from dichloromethane/hexane); mp 219°C; IR (KBr) ν 1678 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60–7.58 (4H, m, arom. H), 7.38–7.33 (4H, m, arom. H), 7.29–7.24 (2H, m, arom. H), 6.89 (2H, s, H-4′), 4.93 (2H, s, $-CH_2-$), 2.53 (6H, s, Ac×2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.9 (2C, C=O), 154.3 (2C, C-5′), 152.8 (2C, C-2′), 129.7 (2C, arom. C), 128.8 (4C, arom. CH), 128.0 (2C, arom. CH), 124.0 (2C, C-3′), 123.8 (4C, arom. CH), 105.1 (2C, C-4′), 29.2 (2C, Ac), 27.4 ($-CH_2-$); MS *m/z* (rel. intensity), 384 (22, M^+), 341 (100), 237 (9), 207 (9), 165 (9), 128 (8), 115 (11), 105 (68), 77 (52), 43 (77). Anal. calcd for $C_{25}H_{20}O_4$: C, 78.11; H, 5.24. Found: C, 78.03; H, 5.21. The crystallographic data deposition number: CCDC 198377.

4.2.2. Bis[3-acetyl-5-(4-fluorophenyl)-2-furyl]methane (2b). Colorless microcrystals (from MeOH); mp 172–174°C; IR (KBr) ν 1676 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49–7.44 (4H, m, arom. H), 6.99–6.93 (4H, m, arom. H), 6.74 (2H, s, H-4′), 4.82 (2H, s, $-CH_2-$), 2.43 (6H, s, Ac×2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.8 (2C, C=O), 162.4 (2C, d, J=247.9 Hz, arom. CF), 154.1 (2C, C-5′), 151.8 (2C, C-2′), 125.9 (2C, d, J=3.7 Hz, arom. C), 125.6 (4C, d, J=8.1 Hz, arom. CH), 124.0 (2C, C-3′), 115.8 (4C, d, J=22.4 Hz, arom. CH), 104.8 (2C, C-4′), 29.2 (2C, Ac), 27.2 ($-CH_2-$). Anal. calcd for $C_{25}H_{18}O_4F_2$: C, 71.42; H, 4.32. Found: C, 71.34; H, 4.26.

4.2.3. Bis[3-acetyl-5-(4-chlorophenyl)-2-furyl]methane (2c). Colorless microcrystals (from MeOH); mp 201–202°C; IR (KBr) ν 1670 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53–7.50 (4H, m, arom. H), 7.34–7.32 (4H, m, arom. H), 6.89 (2H, s, H-4′), 4.92 (2H, s, $-CH_2-$), 2.52 (6H, s, Ac×2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.7 (2C, C=O), 154.3 (2C, C-5′), 151.7 (2C, C-2′), 133.8 (2C, arom. CCl), 129.0 (4C, arom. CH), 128.1 (2C, arom. C), 125.0 (4C, arom. CH), 124.1 (2C, C-3′), 105.6 (2C, C-4′), 29.2 (2C, Ac), 27.3 ($-CH_2-$). Anal. calcd for $C_{25}H_{18}O_4Cl_2$: C, 66.24; H, 4.00. Found: C, 66.14; H, 4.13.

4.2.4. Bis[3-acetyl-5-(4-methylphenyl)-2-furyl]methane (2d). Colorless microcrystals (from MeOH); mp 174–175°C; IR (KBr) ν 1682 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49–7.47 (4H, m, arom. H), 7.17–7.14 (4H, m, arom. H), 6.82 (2H, s, H-4′), 4.91 (2H, s, $-CH_2-$), 2.51 (6H, s, Ac×2), 2.33 (6H, s, Me×2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.9 (2C, C=O), 153.9 (2C, C-5′), 152.9 (2C, C-2′), 137.9 (2C, arom. CMe), 129.4 (4C, arom. CH), 126.9 (2C, arom. C), 123.9 (2C, C-3′), 123.8 (4C, arom. CH), 104.3 (2C, C-4′), 29.2 (2C, Ac), 27.3 ($-CH_2-$), 21.3 (2C, Me). Anal. calcd for $C_{27}H_{24}O_4$: C, 78.62; H, 5.86. Found: C, 78.43; H, 5.87.

4.2.5. Bis[3-acetyl-5-(4-methoxyphenyl)-2-furyl]-methane (2e). Reddish-orange microcrystals (from MeOH); mp 128–129°C; IR (KBr) ν 1676, 1661 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53–7.50 (4H, m, arom. H), 6.90–6.87 (4H, m, arom. H), 6.75 (2H, s, H-4′), 4.90 (2H, s, $-CH_2-$), 3.81 (6H, s, MeO×2), 2.51 (6H, s, Ac×2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.9 (2C, C=O), 159.5 (2C, arom. CO), 153.7 (2C, C-5′), 152.8 (2C, C-2′), 125.3 (4C, arom. CH), 124.0 (2C, C-3′), 122.7 (2C, arom. C), 114.2 (4C, arom. CH), 103.5 (2C, C-4′), 55.3 (2C, MeO×2), 29.2 (2C, Ac), 27.3 ($-CH_2-$). Anal. calcd for $C_{27}H_{24}O_6$: C, 72.96; H, 5.44. Found: C, 72.86; H, 5.60.

4.2.6. 2,4-Bis(3-acetyl-5-phenyl-2-furfuryl)-3-acetyl-5-phenylfuran (4). Colorless microcrystals (from MeOH); mp 127–128°C; IR (KBr) ν 1666 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59–7.56 (4H, m, arom. H), 7.44–7.20 (11H, m, arom. H), 6.89 (1H, s, H-4 or 4′), 6.86 (1H, s, H-4′ or 4), 4.90 (2H, s, $-CH_2-$), 4.68 (2H, s, $-CH_2-$), 2.53 (3H, s, Ac), 2.52 (3H, s, Ac), 2.51 (3H, s, Ac); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.6, 194.2, 194.0 (C=O), 157.8 (C-5), 154.0, 153.5 (C-5′), 153.0, 152.1 (C-2′), 150.8 (C-2), 129.8, 129.7, 129.5 (arom. C), 128.8, 128.7, 128.6 (2C, arom. CH), 128.2, 128.1, 127.7 (arom. CH), 126.8 (2C, arom. CH), 125.0 (C-3), 123.8 (2C, arom. CH), 123.7 (C-3′), 123.5 (2C, arom. CH), 122.9 (C-3′), 114.8 (C-4), 105.2, 105.1 (C-4′), 30.5, 29.3, 29.2 (Ac), 27.9, 24.7 ($-CH_2-$); FAB MS *m/z* (rel. intensity), 583 (30, M+1), 539, (36), 397 (30), 307 (18), 199 (100), 154 (47), 105, 45), 77 (15). Anal. calcd for $C_{38}H_{30}O_6$: C, 78.33; H, 5.19. Found: C, 78.12; H, 5.19.

4.3. Reaction of 1a with trisubstituted furan 3d in the presence of $BF_3{\cdot}Et_2O$

The pentenedione **1a** (108 mg, 0.5 mmol) and 3-acetyl-5-(4-methylphenyl)-2-methylfuran (**3d**, 321 mg, 1.5 mmol) were

dissolved in THF (2 mL) containing water (90 μL, 5.0 mmol), and $BF_3{\cdot}Et_2O$ (1.27 mL, 10 mmol) was added to the mixture. The mixture was stirred at 23°C for 30 min. After normal work-up, the residue was separated by silica gel TLC (Wakogel B-10) using hexane/ethyl acetate (1:1 v/v) as the developing solvent, thus affording the product **5** (103 mg, 49%) which was further purified by recrystallization from methanol.

4.3.1. 4-(3-Acetyl-5-phenyl-2-furfuryl)-3-acetyl-5-(4-methylphenyl)-2-methylfuran (5). Colorless needles (from MeOH); mp 153°C; IR (KBr) ν 1677, 1662 (C═O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51–7.48 (2H, m, arom. H of 4-MeC_6H_4–), 7.46–7.43 (2H, m, arom. H of Ph), 7.32–7.27 (2H, m, arom. H of Ph), 7.25–7.22 (1H, m, arom. H of Ph), 7.21–7.18 (2H, m, arom. H of 4-MeC_6H_4–), 6.87 (1H, s, H-4′), 4.34 (2H, s, –CH_2–), 2.66 (3H, s, Ac), 2.53 (3H, s, Ac), 2.42 (3H, s, Me), 2.35 (3H, s, *Me*–C_6H_4–); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.4, 194.2 (C═O), 158.4 (C-5), 157.0 (C-5′), 151.9 (C-2′), 150.1 (C-2), 129.9 (arom. C), 129.4, 128.7 (2C, arom. CH), 127.7 (arom. CH), 127.3 (arom. C), 126.7 (2C, arom. CH), 123.9 (C-3 or 3′), 123.6 (2C, arom. CH), 123.0 (C-3 or 3′), 114.3 (C-4), 105.3 (C-4′), 30.6, 29.3 (Ac), 24.8 (–CH_2–), 21.3 (Me), 15.5 (*Me*C_6H_4–). Anal. calcd for $C_{27}H_{24}O_4$: C, 78.62; H, 5.86. Found: C, 78.79; H, 5.89.

4.4. BF_3-Catalyzed reaction of pentenediones 1a–e with 2,4-pentanedione[9]

1-Aryl-2-pentene-1,4-diones **1a–e** (1.0 mmol)[8] was dissolved in THF (5 mL), and 2,4-pentanedione (1.03 mL, 10 mmol) and $BF_3{\cdot}Et_2O$ (1.27 mL, 10 mmol) were simultaneously added to the solution. The mixture was stirred at 23°C for 15 min. The reaction was exothermic and the yellow color of the solution turned red. Water (20 mL) and a saturated aqueous solution of sodium hydrogencarbonate (30 mL) were added to the reaction mixture, and the aqueous mixture was extracted with chloroform. The combined extract was washed with water (100 mL), dried over anhydrous $MgSO_4$, and concentrated to dryness. The residue was separated by flash column chromatography (Fuji Silysia BW-300 silica gel) with chloroform as the eluting solvent. The obtained products were further purified by silica gel TLC (Wakogel B-10) using hexane/ethyl acetate (1:1 v/v) as the developing solvent, followed by recrystallization from methanol.

4.4.1. 3-(3-Acetyl-5-phenyl-2-furfuryl)-4-hydroxy-3-penten-2-one (6a). Colorless needles (from MeOH); mp 127°C; IR (KBr) ν 3700–3300 (OH), 1673, 1610 (C═O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 16.88 (1H, OH), 7.58–7.57 (2H, m, arom. H), 7.41–7.36 (2H, m, arom. H), 7.32–7.26 (1H, m, arom. H), 6.85 (1H, s, H-4′), 4.12 (2H, s, –CH_2–), 2.49 (3H, s, Ac), 2.24 (6H, s, Ac×2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.6 (C═O), 192.2 (2C, C-2 and C-4), 158.5 (C-2′), 152.5 (C-5′), 129.5 (arom. C), 128.9 (2C), 128.2, 123.7 (2C) (arom. CH), 122.4 (C-3′), 106.1 (C-3), 105.0 (C-4′), 29.4 (Ac), 26.2 (CH_2), 23.5 (2C, Me); MS *m*/*z* (rel. intensity), 298 (33, M^+), 279 (10), 255 (12), 213 (9), 43 (100). Anal. calcd for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08. Found: C, 72.63; H, 6.08.

4.4.2. 3-[3-Acetyl-5-(4-fluorophenyl)-2-furfuryl]-4-hydroxy-3-penten-2-one (6b). Colorless needles (from MeOH); mp 152.5–153.5°C; IR (KBr) ν 3700–3300 (OH), 1678 (C═O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 16.89 (1H, OH), 7.56–7.51 (2H, m, arom. H), 7.12–7.06 (2H, m, arom. H), 6.79 (1H, s, H-4′), 4.12 (2H, s, –CH_2–), 2.49 (3H, s, Ac), 2.24 (6H, s, Ac×2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.5 (C═O), 192.1 (2C, C-2 and C-4), 162.5 (d, J=248.5 Hz, arom. CF), 158.5 (C-2′), 151.7 (C-5′), 125.9 (d, J=3.1 Hz, arom. C), 125.5 (2C, d, J=8.1 Hz, arom. CH), 122.4 (C-3′), 116.0 (2C, d, J=22.4 Hz, arom. CH), 106.1 (C-3), 104.7 (C-4′), 29.4 (Ac), 26.1 (CH_2), 23.5 (2C, Me); FAB HRMS (acetone-NBA) calcd for $C_{18}H_{17}O_4F$ 316.1111. Found 316.1111.

4.4.3. 3-[3-Acetyl-5-(4-chlorophenyl)-2-furfuryl]-4-hydroxy-3-penten-2-one (6c). Colorless needles (from MeOH); mp 177°C; IR (KBr) ν 3700–3300 (OH), 1675, 1609 (C═O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 16.87 (1H, OH), 7.50–7.48 (2H, m, arom. H), 7.37–7.34 (2H, m, arom. H), 6.84 (1H, s, H-4′), 4.12 (2H, s, –CH_2–), 2.49 (3H, s, Ac), 2.23 (6H, s, Ac×2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.4 (C═O), 192.1 (2C, C-2 and C-4), 158.8 (C-2′), 151.5 (C-5′), 134.0 (arom. C), 129.2 (2C, arom. CH), 128.0 (arom. C), 124.9 (2C, arom. CH), 122.5 (C-3′), 106.0 (C-3), 105.5 (C-4′), 29.4 (Ac), 26.2 (CH_2), 23.5 (2C, Me). Anal. calcd for $C_{18}H_{17}ClO_4$: C, 64.97; H, 5.15. Found: C, 65.16; H, 5.27.

4.4.4. 3-[3-Acetyl-5-(4-methylphenyl)-2-furfuryl]-4-hydroxy-3-penten-2-one (6d). Colorless needles (from MeOH); mp 145–146°C; IR (KBr) ν 3700–3300 (OH), 1679, 1597 (C═O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 16.88 (1H, OH), 7.46–7.44 (2H, m, arom. H), 7.20–7.18 (2H, m, arom. H), 6.78 (1H, s, H-4′), 4.11 (2H, s, –CH_2–), 2.48 (3H, s, Ac), 2.37 (Me), 2.24 (6H, s, Ac×2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.6 (C═O), 192.2 (2C, C-2 and C-4), 158.2 (C-2′), 152.8 (C-5′), 138.2, (arom. C), 129.6 (2C, arom. CH), 126.8 (arom. C), 123.7 (2C, arom. CH), 122.3 (C-3′), 106.2 (C-3), 104.3 (C-4′), 29.4 (Ac), 26.2 (CH_2), 23.5 (2C, Me), 21.3 (Me). Anal. calcd for $C_{19}H_{20}O_4$: C, 73.06; H, 6.45. Found: C, 73.08; H, 6.25.

4.4.5. 3-[3-Acetyl-5-(4-methoxyphenyl)-2-furfuryl]-4-hydroxy-3-penten-2-one (6e). Colorless needles (from MeOH); mp 142–145°C; IR (KBr) ν 3700–3300 (OH), 1675, 1609 (C═O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 16.88 (1H, OH), 7.51–7.48 (2H, m, arom. H), 6.93–6.91 (2H, m, arom. H), 6.70 (1H, s, H-4′), 4.10 (2H, s, –CH_2–), 3.84 (3H, s, MeO), 2.48 (3H, s, Ac), 2.24 (6H, s, Ac×2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.7 (C═O), 192.2 (2C, C-2 and C-4), 159.6 (arom. CO), 157.9 (C-2′), 152.6 (C-5′), 125.2 (2C, arom. CH), 122.5 (arom. C), 122.3 (C-3′), 114.3 (2C, arom. CH), 106.2 (C-3), 103.4 (C-4′), 55.4 (MeO), 29.4 (Ac), 26.1 (CH_2), 23.5 (2C, Me). Anal. calcd for $C_{19}H_{20}O_5$: C, 69.50; H, 6.14. Found: C, 69.46; H, 6.05.

4.4.6. 3-(3-Acetyl-2-methyl-4-phenyl-5-furyl)-4-hydroxy-3-penten-2-one (7a). Colorless needles (from MeOH); mp 59–60°C; IR (KBr) ν 3700–3300 (OH), 1679, 1610 (C═O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 16.75 (1H, OH), 7.37–7.35 (3H, m, arom. H), 7.17–7.14 (2H, m, arom. H), 2.59 (3H, s, Ac), 2.00 (3H, s, Me), 1.92 (6H, s, Ac×2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.1 (C═O), 193.7

(2C, C-2 and C-4), 158.1 (C-2′), 144.7 (C-5′), 132.9 (arom. C), 129.1 (2C), 128.8 (2C), 127.9 (arom. CH), 125.5 (C-4′), 123.3 (C-3′), 103.9 (C-3), 30.8 (Ac), 23.9 (2C, Me), 14.5 (Me); MS *m/z* (rel. intensity), 298 (100, M^+), 279 (71), 255 (75), 241 (52), 237 (44), 213 (75), 195 (47), 153 (38), 128 (28), 115 (28), 77 (25), 43 (100). Anal. calcd for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08. Found: C, 72.66; H, 6.31. The crystallographic data deposition number: CCDC 198379.

4.4.7. 3-[3-Acetyl-4-(4-fluorophenyl)-2-methyl-5-furyl]-4-hydroxy-3-penten-2-one (7b). Colorless liquid; IR (KBr) ν 3700–3300 (OH), 1676 (C–O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 16.76 (1H, OH), 7.14–7.08 (4H, m, arom. H), 2.60 (3H, s, Ac), 2.04 (3H, s, Me), 1.92 (6H, s, Ac×2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.6 (C=O), 193.6 (2C, C-2 and C-4), 162.3 (d, J=247.5 Hz, arom. CF), 158.3 (C-2′), 145.0 (C-5′), 130.8 (2C, d, J=8.1 Hz, arom. CH), 128.9 (d, J=3.2 Hz, arom. C), 124.5 (C-4′), 123.2 (C-3′), 115.9 (2C, d, J=21.1 Hz, arom. CH), 103.7 (C-3), 30.8 (Ac), 23.8 (2C, Me), 14.6 (Me); FAB HRMS (acetone-NBA) calcd for $C_{18}H_{17}O_4F$ 316.1111. Found 316.1115.

4.4.8. 3-[3-Acetyl-4-(4-chlorophenyl)-2-methyl-5-furyl]-4-hydroxy-3-penten-2-one (7c). Colorless needles (from MeOH); mp 138–140°C; IR (KBr) ν 3700–3300 (OH), 1676 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 16.76 (1H, OH), 7.37–7.34 (2H, m, arom. H), 7.11–7.08 (2H, m, arom. H), 2.60 (3H, s, Ac), 2.01 (3H, s, Me), 1.91 (6H, s, Ac×2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.4 (C=O), 193.6 (2C, C-2 and C-4), 158.3 (C-2′), 145.0 (C-5′), 133.9, 131.4 (arom. C), 130.4 (2C), 129.0 (2C) (arom. CH), 124.4 (C-4′), 123.1 (C-3′), 103.6 (C-3), 30.9 (Ac), 23.9 (2C, Me), 14.6 (Me). Anal. calcd for $C_{18}H_{17}ClO_4$: C, 64.97; H, 5.15. Found: C, 64.84; H, 5.28.

4.4.9. 3-[3-Acetyl-4-(4-methylphenyl)-2-methyl-5-furyl]-4-hydroxy-3-penten-2-one (7d). Colorless needles (from MeOH); mp 108°C; IR (KBr) ν 3700–3300 (OH), 1681, 1654, 1639 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 16.73 (1H, OH), 7.18–7.15 (2H, m, arom. H), 7.05–7.02 (2H, m, arom. H), 2.58 (3H, s, Ac), 2.36 (3H, s, Me), 2.00 (3H, s, Me), 1.92 (6H, s, Ac×2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.2 (C=O), 193.6 (2C, C-2 and C-4), 158.0 (C-2′), 144.6 (C-5′), 137.6, 129.9 (arom. C), 129.5 (2C), 128.9 (2C) (arom. CH), 125.5 (C-4′), 123.4 (C-3′), 104.0 (C-3), 30.8 (Ac), 23.9 (2C, Me), 21.2 (*Me*–C_6H_4), 14.4 (Me). Anal. calcd for $C_{19}H_{20}O_4$: C, 73.06; H, 6.45. Found: C, 72.90; H, 6.49.

4.4.10. 3-[3-Acetyl-4-(4-methoxyphenyl)-2-methyl-5-furyl]-4-hydroxy-3-penten-2-one (7e). Colorless needles (from MeOH); mp 138–140°C; IR (KBr) ν 3700–3300 (OH), 1673 (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 16.74 (1H, OH), 7.08–7.05 (2H, m, arom. H), 6.91–6.88 (2H, m, arom. H), 3.82 (3H, MeO), 2.58 (3H, s, Ac), 2.02 (3H, s, Me), 1.92 (6H, s, Ac×2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.2 (C=O), 193.7 (2C, C-2 and C-4), 159.2 (arom. CO), 158.0 (C-2′), 144.6 (C-5′), 130.2 (2C, arom. CH), 125.1 (C-4′), 124.9 (arom. C), 123.4 (C-3′), 114.2 (2C, arom. CH), 104.0 (C55.2 (MeO), 30.8 (Ac), 23.9 (2C, Me), 14.5 (Me). Anal. calcd for $C_{19}H_{20}O_5$: C, 69.50; H, 6.14. Found: C, 69.46; H, 6.05. The crystallographic data deposition number: CCDC 198378 (Fig. 3).

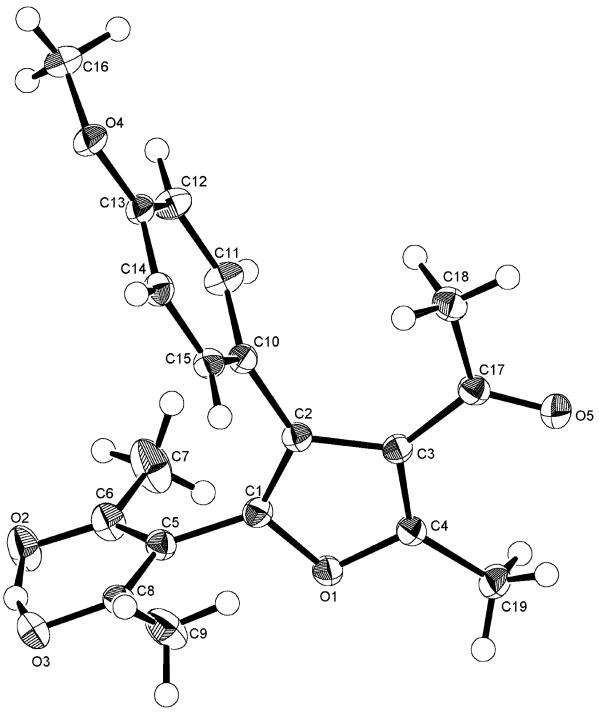


Figure 3. ORTEP drawing of tetrasubstituted furan **7e**.

4.5. Reaction of phenylglyoxal with 2,4-pentanedione in the presence of BF_3·Et_2O

Phenylglyoxal (152 mg, 1.0 mmol) was dissolved in THF (1 mL), and 2,4-pentanedione (1.03 mL, 10 mmol) and BF_3·Et_2O (1.27 mL, 10 mmol) were simultaneously added to the solution. The mixture was stirred at 23°C for 15 min. After the usual work-up, **6a** (111 mg, 37%) and **7a** (166 mg, 56%) were obtained.

4.6. Reaction of 1a with triphenylphosphine

The pentenedione **1a** (108 mg, 0.5 mmol) and triphenylphosphine (197 mg, 0.75 mmol) were dissolved in chloroform (1 mL), and the mixture was heated under reflux for 30 min. Upon cooling, the solvent was removed under reduced pressure, and the residue was separated by silica gel TLC (Wakogel B-10) using chloroform as the developing solvent, thus giving the furan **3a** (88 mg, 88%).

4.7. Treatment of 1a with hydrochloric acid

Concentrated hydrochloric acid (1 mL) was dropwise added to the pentenedione **1a** (216 mg, 1.0 mmol) in THF (1 mL), and the mixture was stirred at 23°C for 30 min. The yellow color of the solution then turned red, and crystals were formed. Water (50 mL) was added to dilute the mixture, and the aqueous mixture was extracted with chloroform. The combined extract was washed with a saturated aqueous solution of sodium hydrogencarbonate and water (50 mL), dried over anhydrous $MgSO_4$, and concentrated to dryness. The residue was separated by flash column chromatography (Fuji Silysia BW-300 silica gel) with chloroform as the eluting solvent, and the 3-acetyl-2-chloromethyl-5-phenylfuran (**8**) was obtained in 87% yield. The product **8** was further purified by recrystallization from dichloromethane/

hexane. The chloromethylfuran **8** (117 mg, 0.5 mmol) was heated under reflux in ethanol (5 mL) for 30 min to quantitatively transform it into 3-acetyl-2-ethoxymethyl-5-phenylfuran (**9**).

4.7.1. 3-Acetyl-2-chloromethyl-5-phenylfuran (8). Colorless needles (from dichloromethane/hexane); mp 128–129°C; IR (KBr) ν 1673 (C═O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71–7.68 (2H, m, arom. H), 7.45–7.39 (2H, m, arom. H), 7.36–7.31 (1H, m, arom. H), 6.87 (1H, s, H-4), 4.98 (2H, s, $-CH_2-$), 2.51 (3H, s, Ac); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.7 (C═O), 154.1 (C-5), 153.2 (C-2), 129.2 (arom. C), 128.9 (2C), 128.7 (arom. CH), 124.9 (C-3), 124.2 (2C, arom. CH), 105.3 (C-4), 36.2 ($-CH_2-$), 29.2 (Ac). Anal. calcd for $C_{13}H_{11}ClO_2$: C, 66.53; H, 4.72. Found: C, 66.54; H, 4.87.

4.7.2. 3-Acetyl-2-ethoxymethyl-5-phenylfuran (9). Colorless oil; IR ($CHCl_3$) ν 1681 (C═O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70–7.67 (2H, m, arom. H), 7.42–7.37 (2H, m, arom. H), 7.32–7.30 (1H, m, arom. H), 6.89 (1H, s, H-4), 4.82 (2H, s, $-CH_2-$), 3.62 (2H, q, J=7.0 Hz, $-CH_2-$), 2.50 (3H, s, Ac), 1.25 (3H, t, J=7.0 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.0 (C═O), 155.7 (C-5), 153.4 (C-2), 129.6 (arom. C), 128.8 (2C), 128.2 (arom. CH), 125.6 (C-3), 124.1 (2C, arom. CH), 105.1 (C-4), 66.3, 63.6 ($-CH_2-$), 29.3 (Ac), 15.2 (Me); FAB HRMS (acetone-NBA) calcd for $C_{15}H_{16}O_3$ 244.1100. Found 244.1099.

4.8. Hydrolysis of 8

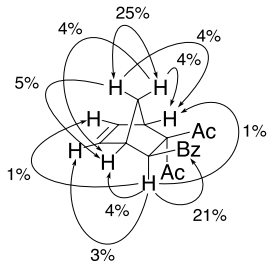
The furfuryl chloride **8** (56.6 mg, 0.24 mmol) was hydrolyzed in a mixture of water (2.5 mL) and tetrahydrofuran (2.5 mL) at the reflux temperature for 3 h to give 3-acetyl-5-phenylfurfuryl alcohol (**10**) in 82% yield. The alcohol **10** (50.7 mg, 0.234 mmol) was allowed to react with $BF_3{\cdot}Et_2O$ (296 μL, 2.34 mmol) in dry THF (2.34 mL) at the reflux temperature for 1 h to yield bis(furyl)methane **2a** in 82% yield.

4.8.1. 3-Acetyl-2-hydroxymethyl-5-phenylfuran (10). Colorless oil; IR (KBr) ν 3600–3100 (OH), 1678 (C═O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68–7.65 (2H, m, arom. H), 7.43–7.38 (2H, m, arom. H), 7.34–7.29 (1H, m, arom. H), 6.87 (1H, s, H-4), 4.80 (2H, s, >CH_2), 4.41 (1H, br, OH), 2.52 (3H, s, Ac); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.3 (>C═O, Ac), 160.1 (>C═, C-2), 152.4 (>C═, C-5), 129.2 (arom. C), 128.7 (2C, arom. CH), 128.2 (arom. CH), 124.6 (>C═, C-3), 123.9 (2C, arom. CH), 105.1 (═CH–, C-4), 57.6 (>CH_2), 28.7 (CH_3, Ac); FAB HRMS (acetone-NBA) calcd for $C_{15}H_{16}O_3$ 216.0786. Found 216.0785.

4.9. Diels–Alder reaction of cyclopentadiene with pentenedione 1a

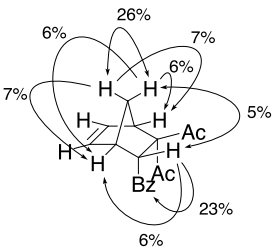
The pentenedione **1a** (108.1 mg, 0.50 mmol) was allowed to react with freshly distilled cyclopentadiene (500 μL, 6.0 mmol) in ethyl acetate (1 mL) at 23°C for 2 h. The yellowish solution decolorized during the reaction. The solvent was removed in vacuo and the residue was separated by silica gel column chromatography (Wako gel C-300) eluting with chloroform to give **11**-*exo* and a mixture of **11**-*endo* and a bicyclic compound **12**. The **11**-*exo* was further purified by recrystallization from dichloromethane/hexane, and the mixture of **11**-*endo* and bicyclic compound **12** was further purified by silica gel column chromatography eluting with chloroform.

4.9.1. *rel*-(1*R*,4*S*,6*S*)-5,5-Diacetyl-6-benzoylbicyclo-[2.2.1]hept-2-ene (11-*exo*). Colorless cubes (from dichloromethane/hexane); mp 94–95°C; IR (KBr) ν 1697, 1674 (C═O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10–8.07 (2H, m, arom. H), 7.63–7.58 (1H, m, arom. H), 7.53–7.48 (2H, m, arom. H), 6.38 (1H, dd, J=5.6, 3.1 Hz, H-2), 6.12 (1H, dd, J=5.6, 2.8 Hz, H-3), 4.65 (1H, d, J=1.6 Hz, H-6), 3.70–3.67 (1H, m, H-4), 2.94–7.90 (1H, m, H-1), 2.21 (1H, dt, J=9.1, 1.6 Hz, H-7), 2.11 (3H, s, Ac), 1.93 (3H, s, Ac), 1.57 (1H, dq, J=9.1, 1.6 Hz, H-7); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.0, 203.3 (>C═O, Ac), 199.9 (>C═O, Bz), 139.8 (═CH–, C-2), 136.9 (arom. C), 135.1 (═CH–, C-3), 133.5, 128.8 (2C), 128.7 (2C) (arom. CH), 79.6 (>C<, C-5), 52.3 (>CH–, C-6), 49.1 (>CH–, C-1), 48.2 (>CH–, C-4), 46.4 (>CH_2, C-7), 29.6, 27.1 (CH_3, Ac); FAB HRMS (acetone-NBA) calcd for $C_{18}H_{19}O_3$ 283.1334 (M+1). Found 283.1336. Anal. calcd for $C_{18}H_{18}O_3{\cdot}1/8H_2O$: C, 75.97; H, 6.37. Found: C, 76.05; H, 6.25.



11-*exo*

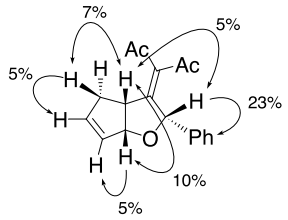
4.9.2. *rel*-(1*R*,4*S*,6*R*)-5,5-Diacetyl-6-benzoylbicyclo-[2.2.1]hept-2-ene (11-*endo*). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07–8.02 (2H, m, arom. H), 7.60–7.45 (3H, m, arom. H), 6.72 (1H, dd, J=5.4, 3.2 Hz, H-3), 5.82 (1H, dd, J=5.4, 2.9 Hz, H-3), 5.39 (1H, d, J=3.7 Hz, H-6), 3.44 (1H, dq, J=3.2, 1.6 Hz, H-4), 3.19–7.15 (1H, m, H-1), 2.23 (3H, s, Ac), 1.88 (3H, s, Ac), 1.41 (1H, dt, J=8.8, 1.7 Hz, H-7), 1.27 (1H, dt, J=8.8, 1.6 Hz, H-7); ^{13}C NMR (75 MHz, $CDCl_3$) δ 204.7, 203.7 (>C═O, Ac), 198.3 (>C═O, Bz), 137.4 (═CH–, C-3), 136.4 (arom. C), 134.0 (═CH–, C-2), 133.2, 128.7 (2C), 128.4 (2C) (arom. CH), 82.0 (>C<, C-5), 53.8 (>CH–, C-6), 49.8 (>CH–, C-4), 48.7 (>CH–, C-1), 45.6 (>CH_2, C-7), 30.1, 26.1 (CH_3, Ac); FAB HRMS (acetone-NBA) calcd for $C_{18}H_{19}O_3$ 283.1334 (M+1). Found 283.1335.



11-*endo*

4.9.3. 4-Diacetylmethylene-3-phenyl-2-oxabicyclo-[3.3.0]oct-7-ene (12). ^{1}H NMR (300 MHz, $CDCl_3$) δ

8.07–8.02 (2H, m, arom. H), 7.60–7.45 (3H, m, arom. H), 6.08 (1H, ddd, J=5.7, 2.7, 1.8 Hz, H-3), 5.97–5.92 (1H, m, H-2), 4.95 (1H, ddd, J=6.5, 2.5, 1.5 Hz, H-1), 4.75 (1H, s, H-7), 2.81–2.71 (1H, m, H-5), 2.57 (1H, dddd, J=16.6, 7.8, 2.7, 1.6 Hz, H-4), 2.31 (3H, s, Ac), 2.28 (3H, s, Ac), 2.36–2.22 (1H, m, H-4); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.7, 197.0, 1 (>C=O, Ac), 168.6 (>C=, C-6), 137.6 (=CH–, C-3), 135.9 (arom. C), 132.8 (arom. CH), 130.7 (=CH–, C-2), 128.5 (2C), 128.5 (2C) (arom. CH), 110.3 (>C=, C-1′), 80.1 (>CH–, C-1), 41.8 (>CH–, C-7), 38.6 (>CH–, C-4), 36.7 (>CH_2, C-3), 30.7, 22.5 (CH_3, Ac); FAB HRMS (acetone-NBA) calcd for $C_{18}H_{19}O_3$ 283.1334 (M+1). Found 283.1335.



12

4.10. X-Ray crystallographic study

All measurements were made using a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo Kα radiation (λ=0.71069 Å). The data reductions were carried out by the PROCESS-AUTO program package, and Lorentz and polarization corrections were performed. Corrections for the secondary extinctions were applied. The structures were solved by the direct method and were refined on SIR-92.[29] The refinements were done by the least-squares full matrix method, with anisotropic displacement parameters for all non-hydrogen atoms. The hydrogen atoms were included but not refined. All calculations were performed using the teXsan[30] crystallographic software package of Molecular Structure Corporation. The crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 198377-198379. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44-0-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk.

5. Supplementary material

X-Ray structural informations for **2a**, **7a**, and **7e** are collected in Tables 3–5. Copies of IR, ^{1}H NMR, ^{13}C NMR, and DEPT spectra for **2a**, **4**, **5**, **6a**, **7a**, **8**, **9**, and **10**; copies of ^{1}H NMR, ^{13}C NMR, DEPT, HH COSY, and HC COSY spectra for **11**-*exo*, a mixture of **11**-*endo* and **12**.

Acknowledgements

This research was supported by Grant-in-Aid for Scientific Research on Priority Areas (A) 'Exploitation of Multi-Element Cyclic Molecules' No. 13029088 and No.14044078, from the Ministry of Education, Culture, Sports, Science and Technology, Japan, and also by a Grant-in-Aid for Scientific Research, No. 13640539, from the Japan Society for the Promotion of Science. We thank Professor Emeritus Kazu Kurosawa, Kumamoto University, Japan, for his helpful discussions and suggestions. We also gratefully acknowledge Professor Teruo Shinmyozu and Dr Mikio Yasutake, Insutitute for Fundamental Research of Organic Chemistry, Kyushu University, Japan, for their crystallographic assistance.

References

1. (a) Dean, F. A. *Naturally Occurring Oxygen Ring Compounds*; Butterworths: London, 1963. (b) *Natural Products Chemistry*; Nakanishi, K., Goto, T., Ito, S., Natori, S., Nozoe, S., Eds.; Kodansha: Tokyo, 1974; Vols. 1–3. 1975, 1983. (c) Dean, F. M. *Advances in Heterocyclic Chemistry*; Katritzky, A. R., Ed.; Academic: New York, 1982; Vol. 30, pp 167–238. (d) Dean, F. M. *Advances in Heterocyclic Chemistry*; Katritzky, A. R., Ed.; Academic: New York, 1983; Vol. 31, pp 237–344.
2. (a) Dunlop, A. P.; Peters, F. N. *The Furans*; Reinhold: New York, 1953. (b) Bosshard, P.; Eugster, C. H. *Advances in Heterocyclic Chemistry*; Katritzky, A. R., Boulton, A. J., Eds.; Academic: New York, 1966; Vol. 7, pp 377–488. (c) Livingstone, R. In *Rodd's Chemistry of Carbon Compounds*; 2nd ed. Coffey, S., Ed.; Elsevier: Amsterdam, 1973; Vol. IV, pp 83–217, Part A, Chapter 2.
3. (a) Corey, E. J.; Cheng, X.-M. *The Logic of Chemical Synthesis*; Wiley: New York, 1989. (b) Nicolaou, K. C.; Sorensen, E. J. *Classics in Total Synthesis*; VCH: Weinheim, 1996.
4. (a) Benassi, R. *Comprehensive Heterocyclic Chemistry II*; Katritzky, A. R., Rees, C. W., Scriven, E. F. V., Eds.; Pergamon: Oxford, 1996; Vol. 2, pp 259–295. (b) Heaney, H.; Ahn, J. S. *Comprehensive Heterocyclic Chemistry II*; Katritzky, A. R., Rees, C. W., Scriven, E. F. V., Eds.; Pergamon: Oxford, 1996; Vol. 2, pp 297–357. (c) Friedrichsen, W. *Comprehensive Heterocyclic Chemistry II*; Katritzky, A. R., Rees, C. W., Scriven, E. F. V., Eds.; Pergamon: Oxford, 1996; Vol. 2, pp 351–393. (d) Keay, B. A.; Dibble, P. W. *Comprehensive Heterocyclic Chemistry II*; Katritzky, A. R., Rees, C. W., Scriven, E. F. V., Eds.; Pergamon: Oxford, 1996; Vol. 2, pp 395–436. (e) Trost, B. M.; Fleming, I. *Comprehensive Organic Synthesis*; Pergamon: Oxford, 1991.
5. (a) Nishino, H. *Bull. Chem. Soc. Jpn* **1985**, *58*, 1922–1927. (b) Nishino, H.; Yoshida, T.; Kurosawa, K. *Bull. Chem. Soc. Jpn* **1991**, *64*, 1097–1107. (c) Qian, C.-Y.; Hirose, J.; Nishino, H.; Kurosawa, K. *J. Heterocycl. Chem.* **1994**, *31*, 1219–1227. (d) Nishino, H.; Nguyen, V.-H.; Yoshinaga, S.; Kurosawa, K. *J. Org. Chem.* **1996**, *61*, 8264–8271. (e) Ouyang, J.; Nishino, H.; Kurosawa, K. *J. Heterocycl. Chem.* **1997**, *34*, 81–86. (f) Nguyen, V.-H.; Nishino, H.; Kurosawa, K. *Synthesis* **1997**, 899–908. (g) Kajikawa, S.; Noiri, Y.; Shudo, H.; Nishino, H.; Kuroswa, K. *Synthesis* **1998**, 1457–1462.
6. (a) Avery, T. D.; Taylor, D. K.; Tiekink, E. R. T. *J. Org. Chem.* **2000**, *65*, 5531–5546. (b) Adam, W.; Balci, M.; Kiliç, H. *J. Org. Chem.* **2000**, *65*, 5926–5931.
7. (a) Adam, W.; Rodriguez, A. *J. Am. Chem. Soc.* **1980**, *102*,

404–406. (b) Graziano, M. L.; Iesce, M. R.; Scarpati, R. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1955–1959. (c) Graziano, M. L.; Iesce, M. R.; Carli, B.; Scarpati, R. *Synthesis* **1982**, 736–738. (d) Graziano, M. L.; Iesce, M. R.; Carli, B.; Scarpati, R. *Synthesis* **1983**, 125–126. (e) Graziano, M. L.; Iesce, M. R.; Chiosi, S.; Scarpati, R. *J. Chem. Soc., Perkin Trans. 1* **1983**, 2071–2074. (f) Graziano, M. L.; Iesce, M. R. *Synthesis* **1984**, 64–66. (g) Graziano, M. L.; Iesce, M. R.; Scarpati, R. *Synthesis* **1984**, 66–68. (h) Iesce, M. R.; Cermola, F.; Graziano, M. L.; Scarpati, R. *J. Chem. Soc., Perkin Trans. 1* **1994**, 147–152. (i) Iesce, M. R.; Cermola, F.; Guitto, A.; Giordano, F. *J. Chem. Soc., Perkin Trans. 1* **1999**, 475–478.

8. (a) Onitsuka, S.; Nishino, H.; Kurosawa, K. *Heterocycl. Commun.* **2000**, *6*, 529–532. (b) Onitsuka, S.; Nishino, H.; Kurosawa, K. *Tetrahedron* **2001**, *57*, 6003–6009.
9. Onitsuka, S.; Nishino, H.; Kurosawa, K. *Tetrahedron Lett.* **2000**, *41*, 3149–3152.
10. (a) Alickmann, D.; Fröhlich, R.; Maulitz, A. H.; Würthwein, E.-U. *Eur. J. Org. Chem.* **2002**, 1523–1537. (b) Lutz, R. E.; Stuart, A. H. *J. Am. Chem. Soc.* **1937**, *59*, 2316–2321. (c) Nowlin, G. *J. Am. Chem. Soc.* **1950**, *72*, 5754–5756.
11. Ishihara, K. In *Lewis Acids in Organic Synthesis*; Yamamoto, H., Ed.; Wiley/VCH: Weinheim, 2000; pp 89–190.
12. (a) Howes, P. D.; Stirling, C. J. M. *Organic Synthesis*; Wiley: New York, 1988; Collect. Vol. 6. pp 31–38. (b) Hendrickson, J. B.; Rees, R.; Templeton, J. F. *J. Am. Chem. Soc.* **1964**, *86*, 107–111. (c) Davies, H. M. L.; Cantrell, Jr. W. R.; Romines, K. R.; Baum, J. S. *Org. Synth.* **1991**, *70*, 93. (d) Marshall, J. A.; Robinson, E. D. *J. Org. Chem.* **1990**, *55*, 3450–3451. (e) Garst, M. E.; Spencer, T. A. *J. Am. Chem. Soc.* **1973**, *95*, 250–252.
13. (a) Gabriele, B.; Salerno, G.; Lauria, E. *J. Org. Chem.* **1999**, *64*, 7687–7692. (b) Gabriele, B.; Salerno, G.; De Pascali, F.; Costa, M.; Chiusoli, G. P. *J. Org. Chem.* **1999**, *64*, 7693–7699. (c) Jeevanandam, A.; Narkunan, K.; Ling, Y.-C. *J. Org. Chem.* **2001**, *66*, 6014–6020. (d) Qing, F.-L.; Gao, W.-Z.; Ying, J. *J. Org. Chem.* **2000**, *65*, 2003–2006. (e) Gilchrist, T. L. *J. Chem. Soc., Perkin Trans. 1* **2001**, 2491–2515.
14. (a) Neilsen, A. T.; Houlihan, W. *J. Org. React.* **1968**, *16*, 1–438. (b) Mukaiyama, T. *Org. React.* **1982**, *28*, 203–331. (c) Takazawa, O.; Kogami, K.; Hayashi, K. *Bull. Chem. Soc. Jpn* **1985**, *58*, 2427–2428. (d) Kawai, M.; Onaka, M.; Izumi, Y. *Bull. Chem. Soc. Jpn* **1988**, *61*, 1237–1245.
15. (a) Johnson, J. R.; Johns, G. *Org. React.* **1967**, *15*, 204–599. (b) Bossio, R.; Marcaccini, S.; Pepino, R.; Torroba, T. *Synthesis* **1993**, 783–785.
16. The structure of **7a** was erroneously assigned as 3-(3-acetyl-2-methyl-5-phenyl-4-furyl)-4-hydroxy-3-penten-2-one based on the spectroscopic data in the preliminary communications.[9]
17. Ciranni, G.; Clementi, S. *Tetrahedron Lett.* **1971**, 3833–3836.
18. (a) Graziano, M. L.; Iesce, M. R.; Carli, B.; Scarpati, R. *Synthesis* **1983**, 125–126. (b) Haddadin, M. J.; Agha, B. J.; Tabri, R. F. *J. Org. Chem.* **1979**, *44*, 494–497. (c) Ramirez, F.; Madan, O. P.; Smith, C. P. *J. Org. Chem.* **1965**, *30*, 2284–2290. (d) Avery, T. D.; Taylor, D. K.; Tiekink, R. T. *J. Org. Chem.* **2000**, *65*, 5531–5546.
19. Adembri, G.; De Sio, F.; Nesi, R.; Scotton, M. *J. Chem. Soc. (C)* **1970**, 1536–1540.
20. (a) Smith, M. B.; March, J. *March's Advanced Organic Chemistry*; Wiley: New York, 2001; pp 1062–1171. (b) Fringuelli, F.; Taticchi, A. *Dienes in the Diels–Alder Reaction*; Wiley: New York, 1990; pp 177–261. (c) Fleming, I. *Pericyclic Reactions*; Oxford University: Oxford, 1999.
21. (a) Alder, K.; Günzl, W. *Chem. Ber.* **1960**, *93*, 809–825. (b) Stockmann, H. *J. Org. Chem.* **1961**, *26*, 2025–2029. (c) Jones, D. W.; Wife, R. L. *J. Chem. Soc., Chem. Commun.* **1973**, 421–422. (d) Smith, J. R. S.; Norman, R. O. C.; Stillings, M. R. *Tetrahedron* **1978**, *34*, 1381–1383.
22. (a) Lutz, R. E.; Rowlett, Jr. R. J. *J. Am. Chem. Soc.* **1948**, *70*, 1359–1363. (b) Dien, C.-K.; Lutz, R. E. *J. Org. Chem.* **1956**, *21*, 1492–1509. (c) Mosterd, A.; Matser, H. J.; Bos, H. J. T. *Tetrahedron Lett.* **1974**, 4179–4180.
23. (a) Ramirez, F.; Madan, O. P.; Smith, C. P. *J. Org. Chem.* **1965**, *30*, 2284–2290. (b) Haddadin, M. J.; Agha, B. J.; Tabri, R. F. *J. Org. Chem.* **1979**, *44*, 494–497.
24. (a) Lutz, R. E.; Bauer, C. R. *J. Am. Chem. Soc.* **1951**, *73*, 3456–3459. (b) Bailey, P. S.; Bath, S. S.; Thomsen, W. F.; Nelson, H. H.; Kawas, E. E. *J. Org. Chem.* **1956**, *21*, 297–303.
25. Lutz, R. E.; Bauer, C. R.; Lutz, R. G.; Gillespie, J. S. *J. Org. Chem.* **1955**, *20*, 218–224.
26. Lutz, R. E.; McGinn, C. E. *J. Am. Chem. Soc.* **1942**, *64*, 2585–2588.
27. (a) Bailey, P. S.; Kawas, E. E.; Smith, L. L. *J. Am. Chem. Soc.* **1951**, *73*, 4088–4090. (b) Bailey, P. S.; Pomerantz, S. H. *J. Am. Chem. Soc.* **1953**, *75*, 281–284.
28. (a) Riley, H. A.; Gray, A. R. *Organic Synthesis*; Wiley: New York, 1966; Collect. Vol. 2, pp 509–511. (b) Mikol, G. J.; Russell, G. A. *Org. Synth.* **1973**, *5*, 937–940.
29. Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A.; Polidori, G. *J. Appl. Crystallogr.* **1994**, *27*, 435.
30. *Crystal Structure Analysis Package*; Molecular Structure Corporation, 1985 and 1992.