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Photooxygenation of 3-acetyl-5-aryl-2-methylfurans via endoperoxide intermediate and the following reactions

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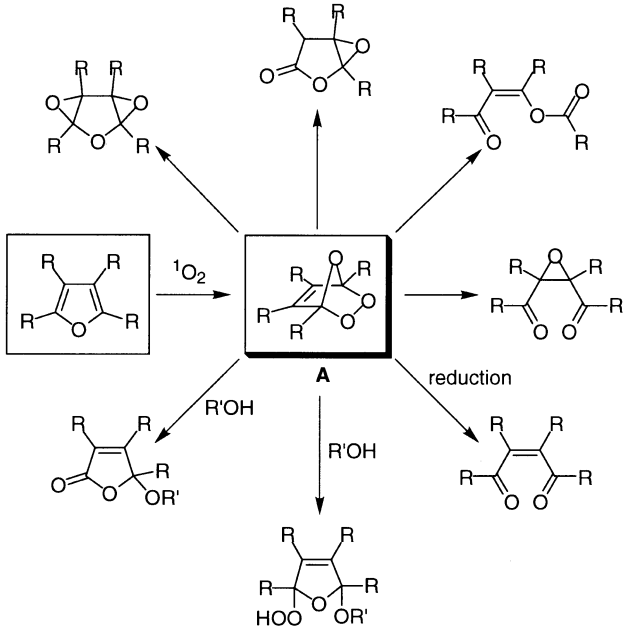
Abstract—The photooxygenation of 3-acetyl-5-aryl-2-methylfurans **1a**–**e** selectively produced 2,2-diacetyl-3-aroyloxiranes **2a**–**e**, 3-acetyl-1-aryl-2-pentene-1,4-diones **3a**–**e**, and 3-acetyl-1-aryl-2-hydroxy-2-pentene-1,4-diones **4a**–**d** via the endoperoxide intermediate A depending on the reaction conditions and the work-up procedure. The oxiranes **2a**–**e** were mainly obtained in 56–77% yields by allowing the reaction mixture to stand at ambient temperature after the irradiation, while the treatment of the reaction mixture with water mainly gave the 1,4-diones **3a**–**e** (62–69%). Heating the reaction mixture at 80°C after the irradiation decreased the total yield of the products, however, the enols **4a**–**d** were newly formed in 8–12% yields. Direct UV irradiation of the endoperoxide intermediate A led to the homolytic fission of the peroxide linkage to produce the same enols **4a**–**e** (16–39%). The self-sensitized photooxygenation of **1a**–**d** using a UV light also gave **4a**–**d** in a similar yield. The reaction pathway is discussed based on these results.

1. Introduction

In recent years, rapid progress has been made in the reaction using singlet oxygen which is an active species in dye-sensitized photooxygenation.[1] In general, furans are allowed to react with singlet oxygen to produce unstable 2,3,7-trioxabicyclo[2.2.1]hept-5-enes **A**,[2] the so-called endoperoxides, which successively rearrange to afford diepoxyfurans,[3–6] epoxylactones,[5,6] enol esters,[4,6–12] and oxiranes,[7–14] while the alcoholysis of **A** yields alkoxybutenolides[6,15,16] and alkoxy-hydroperoxydihydrofurans (Scheme 1).[1,6,15,17] The reduction of **A** produces *cis*-2-butene-1,4-diones (Scheme 1).[5–16,18] The product distribution depends on the reaction conditions and the properties of the substituents on the furan ring.[2–16]

In previous studies, we reported that the oxidation of 1,1-diarylethenes with tris(2,4-pentanedionato)manganese(III) or manganese(III) acetate in the presence of 2,4-pentanedione in boiling acetic acid gave 3-acetyl-5,5-diaryl-2-methyl-4,5-dihydrofurans,[19,20] which were irradiated using a high-pressure mercury lamp to provide 2-acetyl-4-aryl-1-methylnaphthalenes in high yields (Eq. (1) in Scheme 2).[21] On the other hand, a similar reaction at room temperature in air quantitatively yielded 4-acetyl-6,6-diaryl-3-methyl-1,2-dioxan-3-ols,[22] which were easily converted by the acid-catalyzed decomposition to give 3-acetyl-5-aryl-2-methylfurans (Eq. (2) in Scheme 2).[23] The photo-induced benzannulation was so efficient and convenient that it prompted us to investigate the



Scheme 1.

Keywords: photooxygenation; endoperoxide intermediate; UV irradiation.

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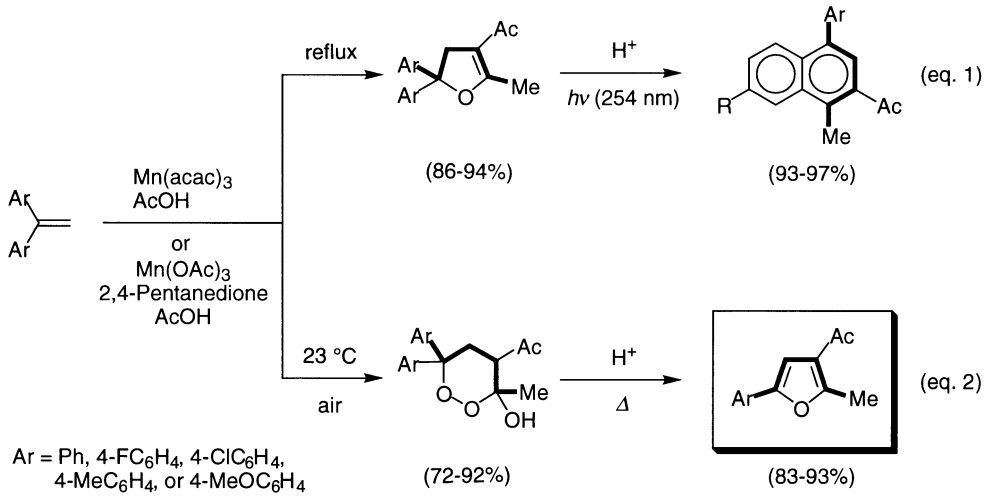


Scheme 2.

photoreaction of furans **1a–e** in expectation of the benz-annulation or [2+2]cycloaddition. However, it was found that furan **1a** was quite sensitive toward singlet oxygen and 2,2-diacetyl-3-benzoyloxirane (**2a**) was obtained in good yield.[14] Although the photooxygenation of the substituted furans is well documented and characterized because of their sensitivity toward singlet oxygen[1] and the importance for the synthesis of industrial and pharmaceutical

Table 1. Photooxygenation of 3-acetyl-5-aryl-2-methylfurans **1a–e**

Entry	Substrate	Sensitizer	Light[a]	Irradiation time (min)	Product (yield/%)[b]		
1[c]	**1a**	None	Visible	15	n.r.[d]		
2[e]	**1a**	Rose Bengal	Visible	5	**2a** (63)	**3a** (9)	**4a** (trace)
3[e]	**1b**	Rose Bengal	Visible	5	**2b** (57)	**3b** (14)	**4b** (trace)
4[e]	**1c**	Rose Bengal	Visible	5	**2c** (56)	**3c** (9)	**4c** (trace)
5[e]	**1d**	Rose Bengal	Visible	5	**2d** (71)	**3d** (10)	
6[e]	**1e**	Rose Bengal	Visible	5	**2e** (77)	**3e** (12)	
7[f]	**1a**	Rose Bengal	Visible	5	**2a** (6)	**3a** (68)	
8[f]	**1b**	Rose Bengal	Visible	5	**2b** (10)	**3b** (62)	
9[f]	**1c**	Rose Bengal	Visible	5	**2c** (8)	**3c** (68)	
10[f]	**1d**	Rose Bengal	Visible	5	**2d** (11)	**3d** (69)	
11[f]	**1e**	Rose Bengal	Visible	5	**2e** (10)	**3e** (67)	
12[g]	**1a**	Rose Bengal	Visible	5	**2a** (31)	**3a** (6)	**4a** (12)
13[g]	**1b**	Rose Bengal	Visible	5	**2b** (28)	**3b** (3)	**4b** (10)
14[g]	**1c**	Rose Bengal	Visible	5	**2c** (27)	**3c** (2)	**4c** (9)
15[g]	**1d**	Rose Bengal	Visible	5	**2d** (46)	**3d** (4)	**4d** (8)
16[g]	**1e**	Rose Bengal	Visible	5	**2e** (79)	**3e** (4)	
17[c]	**1a**	None	UV	15	n.r.[d]		
18[h]	**1a**	Rose Bengal	UV	60	c.m.[i]		
19[j]	**1a**	Rose Bengal	Visible+UV	3+60	**4a** (39)		
20[j]	**1b**	Rose Bengal	Visible+UV	3+60	**4b** (28)		
21[j]	**1c**	Rose Bengal	Visible+UV	3+60	**4c** (38)		
22[j]	**1d**	Rose Bengal	Visible+UV	3+60	**4d** (27)		
23[j]	**1e**	Rose Bengal	Visible+UV	3+60	**4e** (16)		
24[h]	**1a**	None	UV	60	**4a** (34)		
25[h]	**1a**	None	UV	120	**4a** (27)		
26[h]	**1b**	None	UV	60	**4b** (32)		
27[h]	**1c**	None	UV	60	**4c** (36)		
28[h]	**1d**	None	UV	60	**4d** (30)		
29[h]	**1e**	None	UV	60	c.m.[i]		

The photooxygenation of **1** (0.5 mmol) was carried out in acetonitrile (10 mL) at 0°C with dry air bubbling (flow rate: 120 dm^3 min^{-1}).

[a] Visible and UV light were generated by a 250 W halogen lamp and a 100 W high-pressure mercury lamp, respectively.

[b] The yield is based on the amount of the furan **1** used.

[c] The reaction was conducted under an argon atmosphere.

[d] No reaction occurred and **1a** was recovered.

[e] The reaction mixture was kept at 23°C for 12 h after the irradiation (method 1).

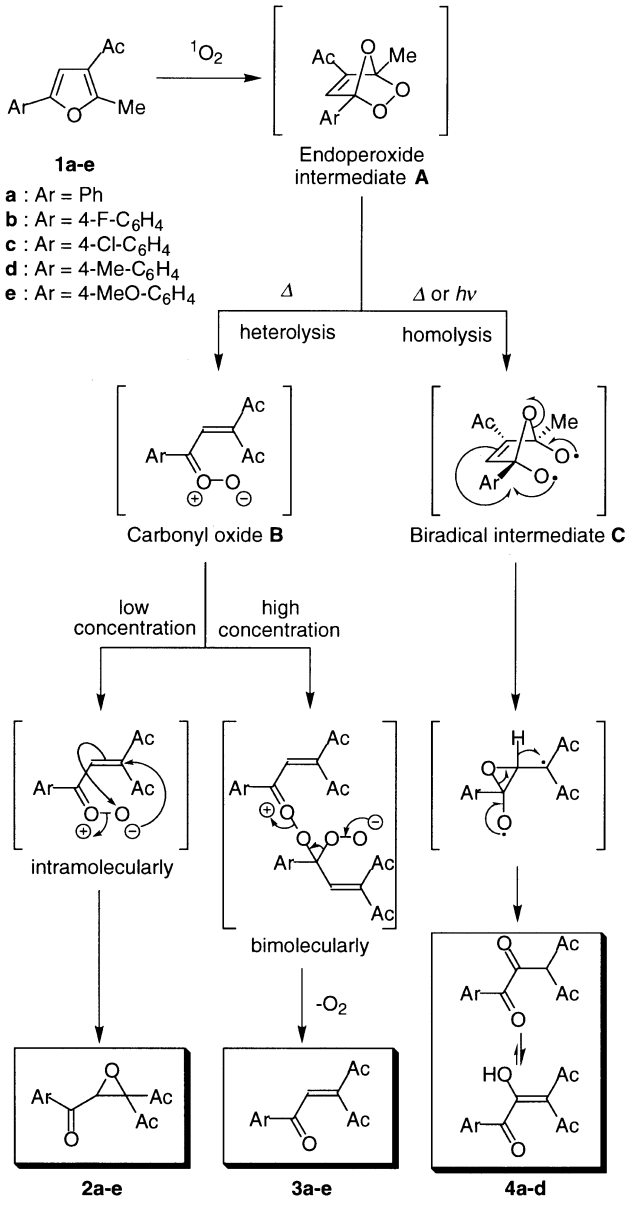
[f] The reaction mixture was poured into water (30 mL) after the irradiation (method 2).

[g] The reaction mixture was warmed to 80°C for 10 min after the irradiation, and then kept at 23°C for 12 h (method 3).

[h] The photooxygenation of **1** (0.2 mmol) was carried out in acetonitrile (10 mL) at 0°C under an air stream moistened with acetonitrile (flow rate: 120 dm^3 min^{-1}).

[i] A complex mixture was obtained.

[j] After the visible irradiation for 3 min, the UV irradiation followed at 0°C for 60 min under an argon atmosphere (method 4).



Scheme 3.

materials,[24] it seems that quite attractive reactions of the furan derivatives still remain. Herein we describe the complete results of the photooxygenation of furans **1a**–**e** and discuss the reaction pathway.[25]

2. Results and discussion

In order to fully understand the photochemistry of the substituted furans, we scrutinized the photooxygenation of furans **1a**–**e** under various reaction conditions. These results are shown in Table 1. First of all, furan **1a** (0.5 mmol) was dissolved in acetonitrile (10 mL) in a quartz cell and irradiated for 15 min under an argon atmosphere using a visible or UV light in the absence of a photosensitizer. However, **1a** was not consumed in either case (Table 1, entries 1, 17). It was suggested that the predicted benzannulation[21] or [2+2]cycloaddition[1] of furan **1a** did not occur or their reaction rates were extremely slow. The reaction of furans **1a**–**e** with singlet oxygen was then investigated. The furan **1a** (0.5 mmol) was dissolved in acetonitrile (10 mL) in a quartz cell containing Rose Bengal (5 mg) and irradiated at 23°C for 5 min using a 250 W halogen lamp under bubbling dry air (flow rate: 120 dm^3 min^{-1}). After the irradiation, the reaction mixture was kept at 23°C for 12 h (method 1), giving 2,2-diacetyl-3-benzoyloxirane (**2a**) in 63% yield together with 3-acetyl-1-phenyl-2-pentene-1,4-dione (**3a**) in 9% yield and a trace amount of 3-acetyl-2-hydroxy-1-phenyl-2-pentene-1,4-dione (**4a**) (Table 1, entry 2 and Scheme 3). The photooxygenation of other 4-fluorophenyl- (**1b**), 4-chlorophenyl- (**1c**), 4-methylphenyl- (**1d**), and 4-methoxyphenyl-substituted furans (**1e**) according to method 1 also gave the corresponding 2,2-diacetyl-3-aroyloxiranes **2b**–**e** in good yields (56–77%) along with a small amount of 2-pentene-1,4-diones **3b**–**e** (9–14%) (Table 1, entries 3–6). A slight substituent effect for the formation of the oxiranes **2a**–**e** was observed. That is, the yield of **2b** and **2c** bearing a halogen atom on the aromatic ring was lower than that of **2a** (Table 1, entries 3, 4), while the yield of **2d** and **2e** having an electron-donating group on the aromatic ring was higher than that of **2a** (Table 1, entries 5, 6). There are many reports in which endoperoxides were rearranged to give epoxides.[3–14,26] The existence of the corresponding endoperoxide intermediate **A** during the photooxygenation was confirmed by the ^{1}H NMR spectrum of the reaction mixture just after irradiation.[4,8,13] The characteristic peak of the methyl group of the endoperoxide intermediate **A** (Ar=Ph) showed at δ 2.05 ppm in the ^{1}H NMR spectrum, while the methyl group of **1a** appeared at δ 2.62 ppm in $CDCl_3$ (see Section 4).[27,28] Since the intermediate **A** was unstable at room temperature, the intermediate **A** would be thermally rearranged to afford the carbonyl oxide intermediate **B** (Scheme 3).[15,29] The electron-deficient carbon–carbon double bond of the intermediate **B** would be intramolecularly oxidized by the carbonyl oxide moiety to give the oxirane **2**.[29–32] The carbonyl oxide moiety should be formed on the aroyl carbonyl group based on the observation of the substituent effect. The carbonyl oxide **B** might be stabilized by the electron-releasing group on the aromatic ring.

The by-products **3a**–**e** were quite interesting due to the extremely electron-deficient alkene and the mechanistic reason for their production.[33] Therefore, in order to improve the yield of **3a**–**e**, the reaction conditions were explored and we found that the treatment of the reaction mixture with water after the irradiation (method 2) led to the selective production of **3a**–**e** in 62–69% yields (Table 1, entries 7–11). The substituent effect was not observed in this case. When the reaction mixture was poured into water, the insoluble materials were instantaneously formed and dissolved in water while the evolution of molecular oxygen was observed. This provided the proof that the endoperoxide intermediate **A** should be immediately rearranged into the carbonyl oxide **B**, and the 2-pentene-1,4-dione **3** was subsequently produced along with the extrusion of molecular oxygen via the bimolecular reaction of **B** (Scheme 3).[12,30] Although the hydrolysis of the carbonyl oxide gives hydroperoxides,[30,33] which are converted to the 2-pentene-1,4-diones by the acid-catalyzed rearrangement,[30] it seems that the dissolution of the acetonitrile solvent into the water resulted in the concentration of **B** to bimolecularly

react. The instability of the 1,4-diones **3a**–**e** under the stated conditions prompted us to convert the stable compounds, and we found that the addition of **3a**–**e** with 2,4-pentanedione in the presence of boron trifluoride gave much more stable furans.[34] Although it was reported that the reduction of the endoperoxide intermediate **A** with diethyl sulfide or the oxidation of the corresponding furans with pyridinium chlorochromate gave the 2-pentene-1,4-diones **3**,[35] the present reaction is much simpler and more convenient for obtaining **3** since such a reductant or an oxidant is not used.

The production of 3-acetyl-1-aroyl-2-hydroxy-2-pentene-1,4-diones **4a**–**c**, which were detected in the reaction at 23°C (Table 1, entries 2–4), was also interesting because of the ambiguous formation mechanism. Since the formation of **4a**–**c** seemed to depend on the reaction temperature, the mixture was simply heated at 80°C for 10 min after the irradiation of **1a** (method 3). As a result, the yield of **2a** (31%) and **3a** (6%) decreased, however, the yield of **4a** slightly increased (12% yield) (Table 1, entry 12). A similar treatment in the reaction of **1b**–**d** also gave **4b**–**d** in ca. 10% yield (Table 1, entries 13–15). The reaction of **1e** according to method 3 led to an increase in the yield of **2e**, however, **4e** was not formed (Table 1, entry 16). Markos and Reusch have shown that the photolysis of an epoxy-ketone afforded 1,3-diketones,[36] so that the oxirane **2** might be rearranged to form the enol **4**. Therefore, **2a** was heated under reflux in acetonitrile for 2 h, however, nothing changed. When the UV irradiation of **2** was also examined in acetonitrile at 23°C, a complex mixture was obtained.

The $n-\sigma^*$ absorption band of the endoperoxide appears near 300 nm and the photolysis causes the homolytic fission of the peroxide bond. Accordingly, the UV irradiation of **1a** in air in the presence of Rose Bengal was investigated in acetonitrile at 0°C for 60 min. However, the reaction did not give **4a**, but a complex mixture containing a small amount of **3a** and benzoic acid (Table 1, entry 18). An activated molecular oxygen probably generated during the reaction might complicate the reaction. Therefore, the endoperoxide intermediate **A** was irradiated under an argon atmosphere using UV light (method 4). After the usual workup, the desired 2-hydroxy-2-pentene-1,4-diones **4a**–**e** were obtained in 16–39% yields (Table 1, entries 19–23). It was proved that the homolytic cleavage of the peroxide linkage resulted in the production of **4**. Although the homolytic reaction of the endoperoxide **A** normally affords diepoxides[3–6] and epoxylactones,[5,6] it is worthnoting that such compounds were not formed during the photooxygenation.

Since it is known that heteroaromatic compounds such as furans also work as a photosensitizer itself, the direct UV irradiation of the furans **1a**–**e** was examined in the absence of the dye sensitizer. The furan **1** (0.2 mmol) was dissolved in acetonitrile (10 mL) in a quartz cell without the photosensitizer and the UV irradiation was carried out at 0°C for 60 min under bubbling of air moistened with acetonitrile (flow rate: 120 dm^3 min^{-1}). As a result, 2-hydroxy-2-pentene-1,4-diones **4a**–**d** were obtained in 30–36% yields (Table 1, entries 24, 26–28). It was again confirmed that the peroxide bond of the endoperoxide **A** was homolytically cleaved to give the 1,4-dione **4** and the substituted furan **1** worked as a self-photosensitizer of singlet oxygen. In all cases except for **1e**, a small amount of **3a**–**d** and the corresponding benzoic acids were also detected in the reaction mixtures based on their ^{1}H NMR spectra.[37] The prolonged UV irradiation led to the decomposition of the products (Table 1, entry 25). The UV irradiation of **1e** did not afford the corresponding 2-hydroxy-2-pentene-1,4-dione, but a complex mixture containing **3e** and *p*-anisic acid (Table 1, entry 29).[37]

3. Conclusion

It was proved that the photooxygenation of the trisubstituted furans **1a**–**e** gave the endoperoxide intermediate **A** which could be rearranged to oxiranes **2a**–**e** at room temperature via the carbonyl oxide **B**, while the aqueous treatment led to the bimolecular reaction of **B** accompanied by the evolution of molecular oxygen to produce 2-pentene-1,4-diones **3a**–**e**. On the other hand, the homolytic scission of the endoperoxide **A** afforded 2-hydroxy-2-pentene-1,4-diones **4a**–**e**. Since the alkenes **3** are also unique, they would be useful as a good synthetic precursor.[34] The self-sensitized photooxygenation of furan **1** would be convenient because of not using a photosensitizer such as a dye sensitizer which normally causes contamination in the reaction system.

4. Experimental

4.1. Measurements

All melting points are uncorrected. All of the ^{1}H- and ^{13}C NMR spectra were recorded at 300 or 400 MHz for the ^{1}H and at 75 or 100 MHz for the ^{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 high resolution mass spectra were measured at the Analytical Center of Kumamoto University, Kumamoto, Japan. Elemental analyses were performed at the Analytical Center of Kumamoto University, Kumamoto, Japan, or the Elemental Analysis Center of Kyushu University, Fukuoka, Japan.

4.2. Materials

The 3-acetyl-5-aryl-2-methylfurans (**1a**–**e**) were prepared according to the literature method.[23] Rose Bengal, acetonitrile, hexane, ethyl acetate, and methanol were purchased from Wako Pure Chemical Ind., Ltd., and were used as received.

4.3. Photooxygenation of furans (method 1)

Furan **1** (0.5 mmol) was dissolved in acetonitrile (10 mL) containing Rose Bengal (5 mg) in a quartz cell and irradiated using a 250 W halogen lamp at 0°C for 5 min with air bubbling from a gas inlet. The flow rate was 120 dm^3 min^{-1}. After standing for 12 h at room temperature, the solvent was removed under reduced pressure and the residue was separated by silica gel TLC (Wakogel B-10) with hexane/ethyl acetate (1:1 v/v) as the developing solvent, thus affording a mixture of **2** and **3**. The ratio and the yields were calculated by the ^{1}H NMR spectra. The

yields are summarized in Table 1. The products **2a**, **2d**, and **2e** were further purified and recrystallized from methanol.

4.3.1. 2,2-Diacetyl-3-benzoyloxirane (2a). Colorless needles (from methanol); mp 91.5–92.0°C (lit,[14] mp 88–90°C); IR ($CHCl_3$) ν 1717, 1693 (C═O); ^{1}H NMR ($CDCl_3$) δ 7.95–7.45 (5H, m, arom H), 4.61 (1H, s, H-3), 2.34 (3H, s, Ac), 2.32 (3H, s, Ac); ^{13}C NMR ($CDCl_3$) 199.7, 199.2, 190.3 (C═O), 134.8 (arom C), 134.7, 129.1 (2C), 128.5 (2C) (arom CH), 69.4 (>C<), 60.6 (>CH-), 28.8, 25.9 (Ac); FABMS *m/z* (rel intensity) 233 (100, M+1), 217 (18), 191 (22), 120 (18), 105 (80). Anal. calcd for $C_{13}H_{12}O_4$: C, 67.23; H, 5.21. Found: C, 67.53; H, 5.51.

4.3.2. 2,2-Diacetyl-3-(4-fluorobenzoyl)oxirane (2b). Colorless oil; IR ($CHCl_3$) ν 1720, 1693 (C═O); ^{1}H NMR ($CDCl_3$) δ 7.99 (2H, m, arom H), 7.19 (2H, m, arom H), 4.55 (1H, s, H-3), 2.34 (3H, s, Ac), 2.33 (3H, s, Ac); ^{13}C NMR ($CDCl_3$) 199.7, 199.1, 188.8 (C═O), 166.6 (d, J=259.2 Hz, arom CF), 131.4 (2C, d, J=11.1 Hz, arom CH), 131.2 (arom C), 116.4 (2C, d, J=22.1 Hz, arom CH), 69.3 (>C<), 60.6 (>CH-), 28.8, 26.0 (Ac); FAB HRMS (MeOH–NBA–NaI) Found: *m/z* 273.0542. Calcd for $C_{13}H_{11}FO_4Na$: M, 273.0539.

4.3.3. 2,2-Diacetyl-3-(4-chlorobenzoyl)oxirane (2c). Colorless oil; IR ($CHCl_3$) ν 1722, 1692 (C═O); ^{1}H NMR ($CDCl_3$) δ 7.88 (2H, m, arom H), 7.48 (2H, m, arom H), 4.54 (1H, s, H-3), 2.33 (3H, s, Ac), 2.31 (3H, s, Ac); ^{13}C NMR ($CDCl_3$) δ 199.5, 199.1, 189.2 (C═O), 141.4, 133.1 (arom C), 129.9 (2C), 129.5 (2C) (arom CH), 69.3 (>C<), 60.6 (>CH-), 28.8, 26.0 (Ac); FABMS *m/z* (rel intensity) 267 (50, M+1), 225 (20), 139 (100). Anal. calcd for $C_{13}H_{11}ClO_4$: C, 58.55; H, 4.16. Found: C, 58.53; H, 4.14.

4.3.4. 2,2-Diacetyl-3-(4-methylbenzoyl)oxirane (2d). Colorless needles (from methanol); mp 70.4°C; IR ($CHCl_3$) ν 1720, 1690 (C═O); ^{1}H NMR ($CDCl_3$) δ 7.84 (2H, m, arom H), 7.30 (2H, m, arom H), 4.57 (1H, s, H-3), 2.43 (3H, s, Me), 2.34 (3H, s, Ac), 2.32 (3H, s, Ac); ^{13}C NMR ($CDCl_3$) 199.8, 199.2, 189.7 (C═O), 146.0, 132.4 (arom C), 129.8 (2C), 128.7 (2C) (arom CH), 69.3 (>C<), 60.8 (>CH-), 28.8, 26.1 (Ac), 21.9 (Me); FABMS *m/z* (rel intensity) 247 (50, M+1), 231 (14), 205 (20), 161 (14), 134 (15), 119 (100). Anal. calcd for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 68.57; H, 5.80.

4.3.5. 2,2-Diacetyl-3-(4-methoxybenzoyl)oxirane (2e). Colorless needles (from methanol); mp 89.5°C; IR ($CHCl_3$) ν 1720, 1681 (C═O); ^{1}H NMR ($CDCl_3$) δ 7.94 (2H, m, arom H), 6.97 (2H, m, arom H), 4.54 (1H, s, H-3), 3.89 (3H, s, MeO), 2.34 (3H, s, Ac), 2.32 (3H, s, Ac); ^{13}C NMR ($CDCl_3$) δ 199.9, 199.2, 188.3 (C═O), 164.8 (arom C), 131.1 (2C, arom CH), 127.9 (arom C), 114.4 (2C, arom CH), 69.3 (>C<), 60.8 (>CH-), 55.7 (MeO), 28.8 (Ac), 26.2 (Ac); FABMS *m/z* (rel intensity) 263 (65, M+1), 221 (18),150 (20), 135 (100). Anal. calcd for $C_{14}H_{14}O_5$: C, 64.12; H, 5.38. Found: C, 64.10; H, 5.47.

4.4. Detection of the endoperoxide A

Furan **1a** (0.5 mmol) was dissolved in acetonitrile (10 mL) containing Rose Bengal (5 mg) in a quartz cell and irradiated using a 250 W halogen lamp at 0°C for 5 min with dry air bubbling. The solvent was removed in vacuo and the ^{1}H NMR spectrum of the residue was immediately measured in deuteriochloroform. The spectrum showed the existence of the endoperoxide **A**. Upon standing for 12 h at 23°C, the spectrum changed to that of the oxirane **2a**.

4.4.1. 5-Acetyl-4-methyl-1-phenyl-2,3,7-trioxabicyclo-[2.2.1]hept-5-ene (A).[27] ^{1}H NMR ($CDCl_3$) δ 7.90–7.35 (5H, m, arom H), 7.20 (1H, s, H-6), 2.35 (3H, s, Ac), 2.05 (3H, s, Me). cf. 3-Acetyl-2-methyl-5-phenylfuran (**1a**)[23] colorless needles (from ethanol); mp 50–51°C (lit,[23] mp 50–51°C); IR ($CHCl_3$) ν 1646 (C═O); ^{1}H NMR ($CDCl_3$) δ 7.41 (5H, m, arom H), 6.80 (1H, s, H-4), 2.62 (3H, s, Me), 2.41 (3H, s, Ac); ^{13}C NMR ($CDCl_3$) δ 193.8 (C═O), 157.6 (C-5), 151.5 (C-2), 129.7 (arom C), 128.6 (2C), 127.6 (2C), 123.5 (arom CH), 123.1 (C-3), 104.9 (C-4), 28.9 (Ac), 14.3 (Me); MS *m/z* (rel intensity) 200 (72, M^+), 185 (87), 157 (39).

4.5. Photooxygenation of furans (method 2)

A similar reaction was carried out using a 250 W halogen lamp at 0°C for 5 min with dry air bubbling (flow rate: 120 $dm^3\ min^{-1}$). After irradiation, the reaction mixture was poured into water (30 mL) at room temperature and a solid precipitated. The solid was dissolved with stirring for 1 h at room temperature, and additional water (50 mL) was added to the aqueous mixture. The extraction with diethyl ether (30×3 mL) followed by flush chromatographic separation on silica gel (Fuji Silysia BW-300 silica gel) with hexane/ethyl acetate (4:1 v/v) gave a mixture of **2** and **3**. The ratio and the yields were determined by the ^{1}H NMR spectra (Table 1). The products **3** were unstable in acetonitrile solution and polymerized at 23°C until 24 h.

4.5.1. 3-Acetyl-1-phenyl-2-pentene-1,4-dione (3a). A pale yellow needle; mp 68.5°C (lit,[14] 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.

4.5.2. 3-Acetyl-1-(4-fluorophenyl)-2-pentene-1,4-dione (3b). Yellow oil; IR ($CHCl_3$) ν 1705, 1668 (C═O), 1605 (C═C–C═O); ^{1}H NMR ($CDCl_3$) δ 8.01 (2H, m, arom H), 7.54 (1H, s,═CH–), 7.19 (2H, m, arom H), 2.46 (3H, s, Ac), 2.44 (3H, s, Ac); ^{13}C NMR ($CDCl_3$) δ 202.7, 195.9, 188.3 (C═O), 166.5 (d, J=257.4 Hz, arom CF), 152.2 (=C<), 132.7 (arom C), 131.6 (2C, d, J=9.2 Hz, arom CH), 129.8 (=CH–), 123.2 (2C, d, J=22.1 Hz, arom CH), 30.7, 27.4 (Ac). FAB HRMS Found: *m/z* 235.0793. calcd for $C_{13}H_{12}FO_3$: M+1, 235.0770.

4.5.3. 3-Acetyl-1-(4-chlorophenyl)-2-pentene-1,4-dione (3c). Yellow oil; IR ($CHCl_3$) ν 1710, 1667 (C═O), 1595 (C═C–C═O); ^{1}H NMR ($CDCl_3$) δ 7.91 (2H, m, arom H), 7.54 (1H, s,═CH–), 7.48 (2H, m, arom H), 2.47 (3H, s, Ac), 2.43 (3H, s, Ac); ^{13}C NMR ($CDCl_3$) δ 202.7, 196.1, 188.7 (C═O), 152.2 (=C<), 141.0, 134.4 (arom C), 130.1 (2C,

arom CH), 129.6 (=CH–), 129.4 (2C, arom CH), 30.7, 27.3 (Ac). FAB HRMS Found: *m/z* 251.0492. Calcd for $C_{13}H_{12}{}^{35}ClO_3$: M+1, 251.0475.

4.5.4. 3-Acetyl-1-(4-methylphenyl)-2-pentene-1,4-dione (3d). Yellow oil; IR ($CHCl_3$) ν 1715, 1675 (C=O), 1615 (C=C–C=O); ^{1}H NMR ($CDCl_3$) δ 7.86 (2H, m, arom H), 7.58 (1H, s,=CH–), 7.30 (2H, m, arom H), 2.46 (3H, s, Ac), 2.42 (6H, s, Me and Ac); ^{13}C NMR ($CDCl_3$) δ 203.0, 196.3, 189.3 (C=O), 151.8 (=C<), 145.7, 133.8 (arom C), 130.2 (=CH–), 129.8 (2C), 128.9 (2C) (arom CH), 30.7, 27.3 (Ac), 21.8 (Me). FAB HRMS Found: *m/z* 231.1022. Calcd for $C_{14}H_{15}O_3$: M+1, 231.1021.

4.5.5. 3-Acetyl-1-(4-methoxyphenyl)-2-pentene-1,4-dione (3e). Yellow oil; IR ($CHCl_3$) ν, 1708, 1660 (C=O), 1600 (C=C–C=O); ^{1}H NMR ($CDCl_3$) δ 7.95 (2H, m, arom H), 7.59 (1H, s,=CH–), 6.97 (2H, m, arom H), 3.88 (3H, s, MeO), 2.46 (3H, s, Ac), 2.42 (3H, s, Ac); ^{13}C NMR ($CDCl_3$) δ 203.1, 196.4, 187.9 (C=O), 164.7 (arom C), 151.6 (=C<), 131.3 (2C, arom CH), 130.3 (=CH–), 129.3 (arom C), 114.3 (2C, arom CH), 55.7 (MeO), 30.8, 27.2 (Ac); FAB HRMS (MeOH–NBA–NaI) Found: *m/z* 269.0772. Calcd for $C_{14}H_{14}O_4Na$: M+Na, 269.0780.

4.6. Photooxygenation of furans (method 3)

After the same irradiation, the reaction mixture was warmed at 80°C for 10 min and them left at room temperature for 12 h. A similar separation according to method A gave **2a–e**, **3a–e**, and **4a–d**. The enols **4a–d** were further purified and recrystallized from benzene.

4.6.1. 3-Acetyl-2-hydroxy-1-phenyl-2-penten-1,4-dione (4a). Colorless needles (from benzene); mp 160°C (decompd); IR (KBr) ν 3400–3000 (OH), 1716, 1640 (C=O); ^{1}H NMR (DMSO-d_6) δ 8.85 (1H, br s, OH), 7.50–7.35 (5H, m, arom H), 2.72 (3H, s, Ac), 2.31 (3H, s, Ac); ^{13}C NMR (DMSO-d_6) δ 196.7, 195.8, 192.6 (C=O), 135.2 (arom C), 129.4, 128.4 (2C), 125.5 (2C) (arom CH), 112.4, 106.1 (=C<), 29.4, 18.2 (Ac); FABMS *m/z* (rel intensity) 233 (43, M+1), 217 (55), 191 (47), 105 (100). Anal. calcd for $C_{13}H_{12}O_4$: C, 67.23; H, 5.21. Found: C, 67.37; H, 5.29.

4.6.2. 3-Acetyl-1-(4-fluorophenyl)-2-hydroxy-2-pentene-1,4-dione (4b). Colorless needles (from benzene); mp 160°C (decompd); IR (KBr) ν 3400–3000 (OH), 1720, 1642 (C=O); ^{1}H NMR (DMSO-d_6) δ 8.91 (1H, br s, OH), 7.51 (2H, m, arom H), 7.30 (2H, m, arom H), 2.71 (3H, s, Ac), 2.31 (3H, s, Ac); ^{13}C NMR (DMSO-d_6) δ 196.7, 195.6, 192.6 (C=O), 162.6 (d, J=246.3 Hz, arom CF), 131.6 (arom C), 127.9 (2C, d, J=9.1 Hz, arom CH), 115.3 (2C, d, J=22.1 Hz, arom CH), 112.3, 105.5 (=C<), 29.4, 18.2 (Ac); FAB HRMS (MeOH–NBA–NaI) Found: *m/z* 273.0583. Calcd for $C_{13}H_{11}FO_4Na$: M+Na, 273.0539.

4.6.3. 3-Acetyl-1-(4-chloropheny)-2-hydroxy-2-pentene-1,4-dione (4c). Colorless needles (from benzene); mp 165°C (decompd); IR (KBr) ν 3300–3000 (OH), 1730, 1655 (C=O); ^{1}H NMR (DMSO-d_6) δ 8.96 (1H, br s, OH), 7.48 (4H, m, arom H), 2.72 (3H, s, Ac), 2.31 (3H, s, Ac); ^{13}C NMR (DMSO-d_6) δ 196.8, 195.4, 192.5 (C=O), 134.2 (2C, arom C), 128.4 (2C), 127.5 (2C) (arom CH), 112.4, 105.4 (=C<), 29.4, 18.2 (Ac); FABMS *m/z* (rel intensity) 267 (50, M+1), 251 (65), 225 (32), 139 (100). Anal. calcd for $C_{13}H_{11}ClO_4$: C, 58.55; H, 4.16. Found: C, 58.62; H, 4.27.

4.6.4. 3-Acetyl-2-hydroxy-1-(4-methylphenyl)-2-pentene-1,4-dione (4d). Colorless needles (from benzene); mp 161°C (decompd); IR (KBr) ν 3300–3000 (OH), 1722, 1648 (C=O); ^{1}H NMR (DMSO-d_6) δ 8.79 (1H, br s, OH), 7.34 (2H, m, arom H), 7.22 (2H, m, arom H), 2.71 (3H, s, Ac), 2.31 (6H, s, Me and Ac); ^{13}C NMR (DMSO-d_6) δ 196.6, 195.9, 192.6 (C=O), 138.9, 132.4 (arom C), 128.9 (2C), 125.4 (2C) (arom CH), 112.4, 106.3 (=C<), 29.5 (Ac), 20.7 (Me), 18.2 (Ac); FABMS *m/z* (rel intensity) 247 (20, M+1), 230 (28), 205 (20), 119 (100). Anal. calcd for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 68.39; H, 5.86.

4.7. Photooxygenation of furans (method 4)

The irradiation of furans **1a–e** (0.2 mmol) in acetonitrile (10 mL) in a quartz cell containing Rose Bengal (5 mg) was conducted at 0°C for 3 min using a 250 W halogen lamp with dry air bubbling (flow rate: 120 dm^3 min^{-1}). After the visible irradiation, the atmosphere in the reaction mixture was thoroughly substituted by argon for 2 min, and then the UV irradiation of the reaction mixture was performed at 0°C for 60 min using a 100 W high-pressure mercury lamp. The solvent was removed in vacuo and the residue was separated by flash column chromatography (Fuji Silysia BW-300 silica gel) with chloroform, giving the 2-hydroxy-2-pentene-1,4-diones **4a–e** (Table 1). The enols **4a–e** were further purified and recrystallized from benzene.

4.7.1. 3-Acetyl-2-hydroxy-1-(4-methoxylphenyl)-2-pentene-1,4-dione (4e). Colorless needles (from benzene); mp 160°C (decompd); IR (KBr) ν 3400–3000 (OH), 1721, 1650 (C=O); ^{1}H NMR (DMSO-d_6) δ 8.74 (1H, br s, OH), 7.36 (2H, m, arom H), 6.96 (2H, m, arom H), 3.76 (3H, s, MeO), 2.70 (3H, s, Ac), 2.31 (3H, s, Ac); ^{13}C NMR (DMSO-d_6) δ 196.5, 196.0, 192.8 (C=O), 160.1, 127.3 (arom C), 127.0 (2C), 113.8 (2C) (arom CH), 112.4 (=C<), 55.2 (MeO), 29.5, 18.3 (Ac). Anal. calcd for $C_{14}H_{14}O_5$: C, 64.12; H, 5.38. Found: C, 64.26; H, 5.52.

4.8. Self-sensitized photooxygenation of furans

The irradiation of furans **1a–e** (0.2 mmol) in acetonitrile (10 mL) in a quartz cell was carried out at 0°C for 60 min using a 100 W high-pressure mercury lamp with bubbling air moistened with acetonitrile (flow rate: 120 dm^3 min^{-1}). The solvent was removed under reduced pressure and the residue was separated by flash column chromatography (Fuji Silysia BW-300 silica gel) with chloroform, giving the 2-hydroxy-2-pentene-1,4-diones **4a–d** except for **4e** and a complex mixture containing a small amount of **3a–e** and the corresponding benzoic acids.

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