Tetrahedron 65 (2009) 3745–3752

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Formation of 1,2-dioxolanes using Mn(III)-based reaction of various arylacetylenes with 2,4-pentanedione and related reaction

Takuma Tsubusaki, Hiroshi Nishino *

Department of Chemistry, Graduate School of Science and Technology, Kumamoto University, Kurokami 2-39-1, Kumamoto 860-8555, Japan

ARTICLE INFO

Article history:
Received 27 November 2008
Received in revised form 17 February 2009
Accepted 17 February 2009
Available online 25 February 2009

Dedicated to Professor Emeritus Kazu Kurosawa, Kumamoto University, Japan, and the Late Professor Jay K. Kochi, University of Houston, USA

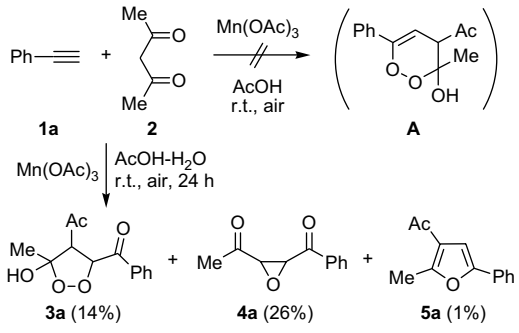
Keywords:
1,2-Dioxolane
Cyclic peroxides
Manganese(III) acetate
Aerobic oxidation
Oxirane

ABSTRACT

The manganese(III)-based aerobic oxidation of arylacetylenes with 2,4-pentanedione at ambient temperature unexpectedly gave the 1,2-dioxolane derivatives in moderate yields together with a small amount of the oxiranes. The 1,2-dioxolanes underwent silica gel-assisted contraction to quantitatively give the oxiranes. The reaction pathway for the formation of the 1,2-dioxolanes and the by-product was discussed.

1. Introduction

A number of cyclic peroxides have been isolated from natural sources[1] and some of them exhibit significant biological activities,[1] such as antitumor,[1b,2] antimalarial,[3] antifungal,[4] antibacterial,[1b] cytotoxic,[1a,5] and antifeedant properties.[1a] Recently, we developed the manganese(III)-catalyzed aerobic peroxidation reaction using 1,3-dicarbonyl compounds with alkenes to produce 1,2-dioxanes.[6] In connection with our study, we have preliminarily reported the aerobic oxidation of phenylacetylene (**1a**) with 2,4-pentanedione (**2**) in the presence of manganese(III) acetate at room temperature.[7] In the reaction, contrary to our expectation, 1,2-dioxolane **3a**, oxirane **4a**, and furan **5a** were isolated instead of 3,4-dihydro-1,2-dioxin-3-ol **A** (Scheme 1). Although many 1,2-dioxolane syntheses are known[8] and many manganese(III)-based cyclization of unsaturated compounds containing the carbon–carbon triple bond have been reported,[9] we are interested in the unusual formation of 1,2-dioxolane **3a** using the manganese(III)-catalyzed aerobic oxidation system. Therefore, in order to verify the reproducibility of the formation of **3a**, optimize the reaction, and elucidate the mechanism for the formation of these products, the reaction was evaluated under various reaction conditions.



Scheme 1.

2. Results and discussion

A mixture of phenylacetylene (**1a**) (1 mmol), 2,4-pentanedione (**2**) (5 mmol), and manganese(III) acetate (2.5 mmol) was stirred in glacial acetic acid at 23 °C in air for 24 h until **1a** was completely consumed. After work-up, the solidified 1,2-dioxolane **3a** (19%) was

* Corresponding author. Tel./fax: +81 96 342 3374.
E-mail address: nishino@sci.kumamoto-u.ac.jp (H. Nishino).

0040-4020/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2009.02.045

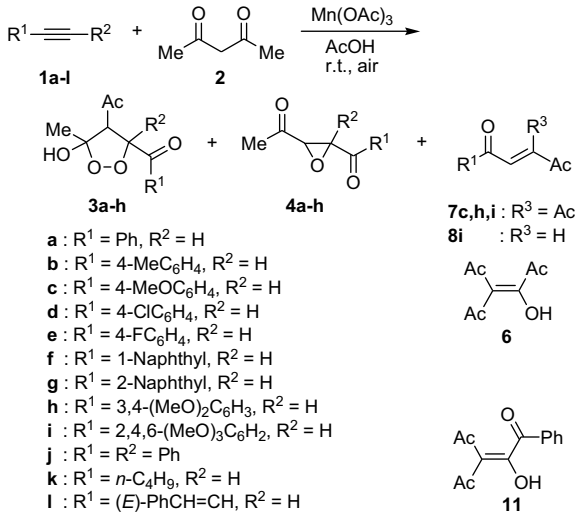
filtered off and the oxirane **4a** (5%) was obtained from the filtrate by silica gel thin-layer chromatographic separation (Table 1, entry 1). The furan **5a** was not detected at all under the reaction conditions. The structural assignments of **3a** and **4a** were based on their ^{1}H NMR, ^{13}C NMR, and IR spectra, as well as their elemental analyses.[7] Longer reaction times led to a decrease in the product yield (Table 1, entries 3, 14, and 25). To promote the reaction, dry air was bubbled through the reaction mixture, however, the reaction was complicated and the product yield decreased (Table 1, entries 4, 5, and 12). When the reaction was carried out using an excess amount of reagents, the highest yield of dioxolane **3a** (45%) was achieved along with the by-products **4a** (5%) and **11** (2%) (Table 1, entry 24). In order to improve the yield of **3a**, the reaction times and the molar ratio of **2** and the oxidant were further examined. Although all the attempts failed, it was found that the reaction was quite sensitive to the reaction temperature. In addition, a small amount of 3-acetyl-4-hydroxyhex-3-ene-2,5-dione (**6**) (1–3%),[10] which could be formed by the radical dimerization of two diacetylmethyl radicals followed by further oxidation,[10b] was also isolated in all the reactions. The reaction of **1a** with 3-methyl-2,4-pentanedione was also conducted, however, the corresponding 1,2-dioxolan-3-ol was not detected but only an intractable mixture was obtained. Although only a catalytic amount of manganese(III) acetate is sufficient for the aerobic peroxidation of alkenes using 1,3-dicarbonyl compounds,[6] the present reaction needed a large amount of **2** and manganese(III) acetate to increase the yield of **3a**. This would be probably attributed to the lower reactivity of the alkynes toward the manganese(III)–enolate complex than that of the alkenes[11] since the ionization potential of the carbon–carbon triple bond is much higher than that of the carbon–carbon double bond,[12,13a] which could be considered as one of the reasons why the yield of the manganese(III)-based reactions involving the oxidative addition of alkynes to 1,3-dicarbonyl compounds remains moderate in many cases.[9e,13b–d]

We next explored the reaction of other acetylenes **1b–l** with 2,4-pentanedione (**2**) under the same conditions (Scheme 2 and Table 2). The use of 1-arylacetylenes **1b–h** resulted in the corresponding 1,2-dioxolanes **3b–h** in comparable yields together with the oxiranes **4b–h** (Table 2, entries 2–8), while the reaction of 2,4,6-trimethoxyphenylacetylene (**1i**) did not afford the desired 1,2-dioxolane, but the pent-2-ene-1,4-diones **7i** and **8i** were obtained (Table 2, entry 9). The pent-2-ene-1,4-diones **7c** and **7h** were also isolated in low yields from the reaction of the methoxyphenyl-substituted acetylenes **1c** and **1h** (Table 2, entries 3 and 8). The reaction of diphenylacetylene (**1j**) and 1-hexyne (**1k**) did not give any products (Table 2, entries 10 and 11). Furthermore, the reaction of (*E*)-2-phenylvinylacetylene (**1l**) gave an intractable mixture (Table 2, entry 12).

Table 1
Reaction of phenylacetylene (**1a**) with 2,4-pentanedione (**2**) in the presence of manganese(III) acetate[a]

Entry	**1a**/**2**/Mn(III)	Temp/°C	Time/h	Product (yield/%)[b]	
				3a	**4a**
1	1:5:2.5	23	24	19	5
2[c]	1:5:2.5	23	24	5	10
3	1:5:2.5	23	36	16	4
4[d]	1:5:2.5	23	12	4	4
5[d]	1:5:2.5	23	24	3	3
6[e]	1:5:2.5	23	24	6	1
7	1:10:2.5	23	24	12	4
8	1:5:5	23	24	20	7
9	1:7.5:5	23	24	20	12
10	1:7.5:5	18	24	11	9
11	1:10:5	23	24	38	6
12[d]	1:10:5	23	24	8	5
13	1:10:5	30	24	12	12
14	1:10:5	23	48	17	14
15[f]	1:10:5	23	24	18	11
16	1:10:5:2.5[g]	23	24	19	12
17	1:10:5:1[h]	23	24	23	6
18	1:10:5:1[i]	23	24	10	2
19[j]	1:10:5	23	24	0	14
20	1:5:7.5	23	24	27	7
21	1:7.5:7.5	23	24	25	7
22	1:10:7.5	23	24	41	4
23	1:5:10	23	24	21	7
24[k]	1:10:10	23	24	45	5
25	1:10:10	23	36	37	9
26	1:12.5:10	23	24	37	6
27	1:10:12.5	23	24	39	9
28	1:12.5:12.5	23	24	37	4

[a] The reaction was carried out in glacial acetic acid (30 mL) in air.
[b] The yield was based on the amount of **1a** used.
[c] After the reaction, acetic acid was removed under reduced pressure at 50 °C prior to the work-up.
[d] The reaction was carried out at 23 °C in glacial acetic acid (30 mL) under a dry air stream.
[e] Water (1 mL) was added.
[f] Ac_2O (1 mL) was added.
[g] Ratio **1a**/**2**/$Mn(OAc)_3$/$Mn(OAc)_2$.
[h] Ratio **1a**/**2**/$Mn(OAc)_3$/$KMnO_4$.
[i] Ratio **1a**/**2**/$Mn(OAc)_2$/$KMnO_4$.
[j] Sodium acetate (10 mmol) was added.
[k] 3-Acetyl-2-hydroxy-1-phenylpent-2-ene-1,4-dione (**11**) (2%) was also isolated.

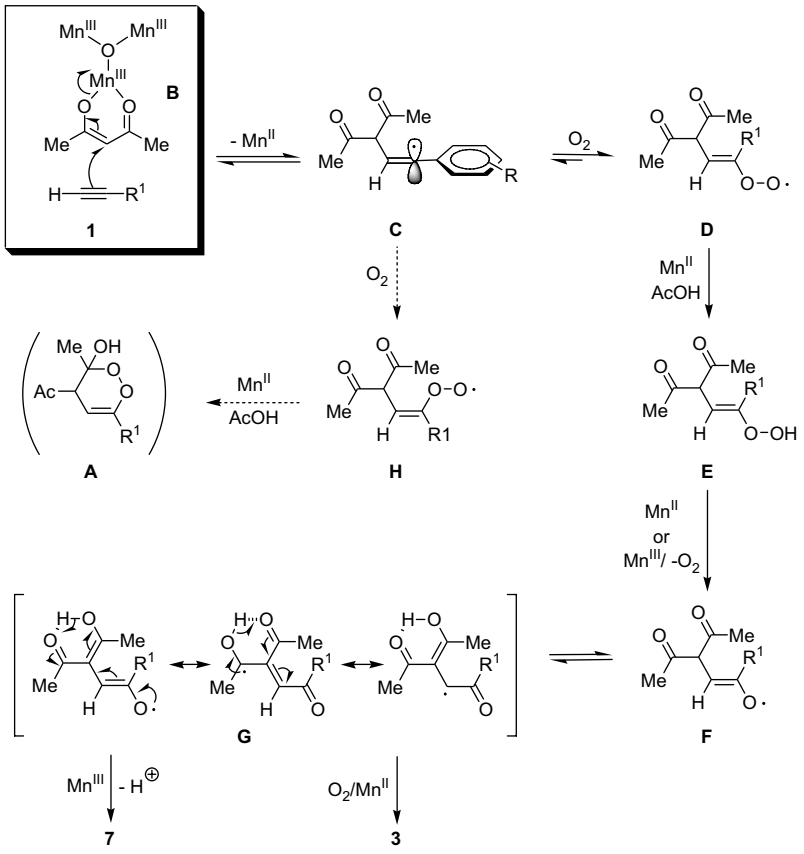


Scheme 2.

Table 2
Reaction of acetylenes **1a–l** with 2,4-pentanedione (**2**) in the presence of manganese(III) acetate[a]

Entry	Acetylene	Product (yield/%)[b]			
1	**1a**	**3a** (45)	**4a** (5)		
2	**1b**	**3b** (52)	**4b** (7)		
3	**1c**	**3c** (64)	**4c** (2)	**7c** (4)	
4	**1d**	**3d** (38)	**4d** (2)		
5	**1e**	**3e** (41)	**4e** (6)		
6	**1f**	**3f** (54)	**4f** (6)		
7	**1g**	**3g** (52)	**4g** (8)		
8	**1h**	**3h** (34)	**4h** (11)	**7h** (9)	
9	**1i**			**7i** (27)	**8i** (6)
10	**1j**	No reaction			
11	**1k**	No reaction			
12	**1l**	Intractable mixture			

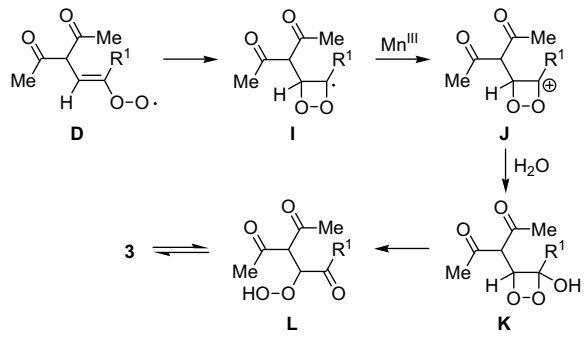
[a] The reaction was carried out at 23 °C for 24 h in glacial acetic acid (30 mL) in air at the molar ratio of **1**/**2**/$Mn(OAc)_3$=1:10:10.
[b] The yield was based on the amount of **1**.



Scheme 3.

The formation of 1,2-dioxolane **3** could be accounted for by a plausible reaction pathway outlined in Scheme 3. In the case of the manganese(III) oxidation, the ligand-exchange reaction of acetate ligands on manganese(III) acetate with 2,4-pentanedione must occur during the first stage to form the manganese(III)–enolate complex **B**.[10b,14] The arylacetylene **1** attacks the enolate complex **B** to give the sp-hybridized linear vinyl radical **C**.[15] The vinyl radical **C** would prefer to be trapped by the dissolved molecular oxygen on the side opposite to the introduced diacetylmethyl group, that is, the molecular oxygen trapping preferentially occurs on the less-hindered face of the vinyl radical **C**.[16] In general, the rate of trapping vinyl radicals by molecular oxygen is very fast as well as other carbon-centered radicals.[17] The potential energy of the resulting vinylperoxy adduct **D** should be considerably lower than that of the vinyl radical **C**, thus the reverse reaction back to **C** possesses a high energy barrier (ca. 40 kcal mol^{-1} in the unsubstituted vinyl radical).[18] Accordingly, the reverse reaction of the vinylperoxy radical **D** back to the vinyl radical **C** would be suppressed. The resulting vinylperoxy radical **D** would be reduced by manganese(II) species followed by protonation to give the hydroperoxide **E**. Because of the geometrical restriction, the hydroperoxide **E** could not cyclize and would be obliged to undergo a redox decomposition[19] and/or Russell-type termination,[8q,20] affording the vinyloxy radical **F**. It should be delocalized (**G**) and finally attacked again by the dissolved molecular oxygen at the α-benzoyl position, producing the corresponding dioxolane **3**. It could not be ruled out the formation of the dihydrodioxinol **A** via the vinylperoxy radical **H** since the total isolated yield of the products was moderate (Table 2), and the formed dihydrodioxinol **A** might be unstable and decompose to afford unidentified products under the reaction conditions. However, any direct evidence for the formation of the dihydrodioxinol **A** could not be obtained from the present work.[21]

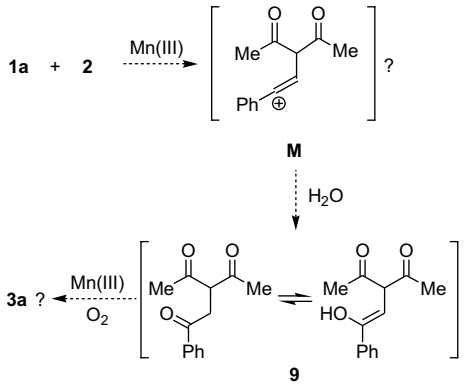
An alternative reaction pathway would be presumed as shown in Scheme 4. The 1,2-dioxetanyl radical **I** might be generated by the intramolecular addition of the vinylperoxy radical **D**. The 1,2-dioxetanyl radical **I** might then be oxidized by manganese(III) acetate followed by attacking with water to give 1,2-dioxetan-3-ol **K**. The 1,2-dioxetan-3-ol **K** might undergo ring-opening to afford hydroperoxyketone **L**, which should readily cyclize to give the dioxolane **3**. However, the 4-*endo-trig* cyclization of the vinylperoxy radical **D** is unlikely because of the high energy barrier.[18] Therefore, the former reaction pathway in Scheme 3 is preferred as the most likely explanation for the formation of the dioxolane **3**. In addition, the pent-2-ene-1,4-diones **7** could be formed by further oxidation of the delocalized alkoxy radicals **G** followed by deprotonation. The



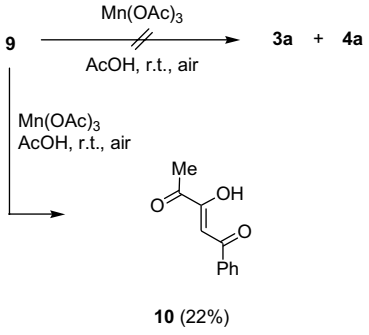
Scheme 4.

electoronic effect from the methoxy-substituted aromatic ring probably caused the formation of the pent-2-ene-1,4-diones **7**.

In a preliminary study,[7] adding a small amount of water to the reaction mixture caused an increase in the yield. It was suggested that the intermediate **9** formed by the reaction of the vinyl cation intermediate **M** with water might be involved during the reaction and further oxidized to afford **3a** (Scheme 5). However, the reproducibility of increasing the product yield was not observed under the same conditions (Table 1, entry 6). Hence, in order to verify the formation of the plausible intermediate **9** derived from the vinyl cation **M**, the 1,4-pentanedione **9** was alternatively prepared and allowed to react under the same aerobic oxidation conditions. However, the desired **3a** and **4a** were not formed, but 3-hydroxy-1-phenylpent-2-ene-1,4-dione (**10**) was isolated in a low yield (Scheme 6). This indicates that the 1,4-pentanedione **9** was not the



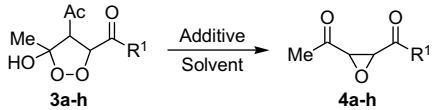
Scheme 5.



Scheme 6.

real intermediate during the aerobic oxidation and, therefore, the possible formation of the vinyl cation **M** could be ruled out.[9d,11]

The formation of the oxiranes **4** deserves comment. Since the dioxolanes **3** seemed to be decomposed to produce the corresponding oxiranes **4**, the dioxolane **3a** was stirred in glacial acetic acid at 23 °C for 24 h (Scheme 7). As a result, **4a** was obtained in an 18% yield along with a 74% recovery of **3a** (Table 3, entry 1). The reaction of **3a** in glacial acetic acid at 23 °C for 48 h in the presence of manganese(II) acetate gave **4a** in a 39% yield together with a 48% recovery of **3a** (Table 3, entry 3). It was suggested that **4a** must be formed by the



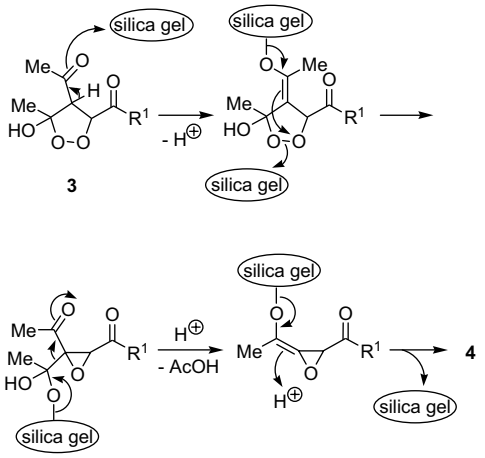
Scheme 7.

Table 3
Conversion of dioxolanes **3** into oxiranes **4**

Entry	3	Additive	Solvent	Temp/°C	Time/h	Rec 3/%	Oxirane[a] 4/%
1	**3a**	None	AcOH	23	24	74	**4a** (18)
2	**3a**	None	AcOH	23	48	57	**4a** (32)
3[b]	**3a**	$Mn(OAc)_2$	AcOH	23	48	48	**4a** (39)
4[b]	**3a**	$Mn(OAc)_2$	AcOH	30	24	32	**4a** (59)
5[c]	**3a**	$HClO_4$	MeCN	23	1	60	**4a** (34)
6[c]	**3a**	$HClO_4$	MeCN	Reflux	0.25	0	**4a** (trace)
7[d]	**3a**	Silica gel	MeCN	23	24	55	**4a** (45)
8[d]	**3a**	Silica gel	Me_2CO	23	24	67	**4a** (33)
9[d]	**3a**	Silica gel	$CHCl_3$	23	24	34	**4a** (66)
10[d]	**3a**	Silica gel	AcOH	23	12	85	**4a** (10)
11[d]	**3a**	Silica gel	MeOH	23	12	0	**4a** (quant)
12[d]	**3b**	Silica gel	MeOH	23	12	0	**4b** (quant)
13[d]	**3c**	Silica gel	MeOH	23	12	0	**4c** (quant)
14[d]	**3d**	Silica gel	MeOH	23	12	0	**4d** (quant)
15[d]	**3e**	Silica gel	MeOH	23	12	0	**4e** (quant)
16[d]	**3f**	Silica gel	MeOH	23	12	0	**4f** (quant)
17[d]	**3g**	Silica gel	MeOH	23	12	0	**4g** (quant)
18[d]	**3h**	Silica gel	MeOH	23	12	0	**4h** (quant)

[a] The yield was based on the ^1H NMR integration.
[b] The reaction was conducted at the molar ratio of **3** (0.2 mmol)/$Mn(OAc)_2$=1:5.
[c] The reaction of **3** (0.2 mmol) was carried out in MeCN (10 mL) containing a 60% $HClO_4$ (0.5 mL).
[d] The reaction of **3** (0.1 mmol) was carried out in the solvent (10 mL) in the presence of silica gel (0.5 g).

decomposition of **3a** during the aerobic oxidation. In order to directly convert **3a** into **4a** during the aerobic oxidation, several attempts have been carried out under various conditions. However, the produced **4a** was also decomposed in situ and the efficient transformation of **3a** into **4a** under the aerobic conditions failed. Interestingly, when the crude product of **3a** was purified by thin-layer chromatography (silica gel), no **3a** was obtained at all, but only **4a** was isolated. It clearly showed that **3a** must be converted into **4a** on the silica gel. In fact, it was confirmed by the treatment of **3a** with silica gel (Table 3, entries 7–10). Incidentally, it was found that methanol was the most appropriate solvent for the silica gel-mediated decomposition reaction (Table 3, entry 11). A similar treatment of other dioxolanes **3b**–**h** with silica gel in methanol quantitatively gave the corresponding oxiranes **4b**–**h** (Scheme 7, Table 3, entries 12–18). Nevertheless, the dioxolanes **3a**–**h** were thermally stable at ambient temperature even after a long-term storage in air. Although there were several reports describing the conversion of 1,2-dioxolan-3-ols into oxiranes under alkaline conditions,[8u,22] to the best of our knowledge, the conversion of the dioxolanes **3** into the oxiranes **4** mediated by silica gel has never been reported. A plausible pathway for the formation of **4** is depicted in Scheme 8.



Scheme 8.

3. Conclusion

Various 1,2-dioxolanes **3a**–**h** were obtained by the manganese(III)-mediated aerobic oxidation of arylacetylenes **1a**–**h** only in moderate yields, although many efforts to improve the yield have been done. The reaction pathway for the formation of the dioxolanes **3** was explained on the basis of the molecular oxygen trapping of the vinyl radical **C** and the decomposition of the hydroperoxide intermediate **E**. Furthermore, it was found that the dioxolanes **3** were quantitatively transformed into the corresponding oxiranes **4** in the presence of silica gel in methanol.

4. Experimental

4.1. General

The NMR spectra were recorded using a JNM EX300 FT NMR spectrometer at 300 MHz for ^{1}H and at 75 MHz for ^{13}C, with tetramethylsilane as the internal standard. The chemical shifts are reported in δ values (ppm). The IR spectra were measured by a Shimazu 8400 FT IR spectrophotometer, and expressed in cm^{-1}. The EIMS spectra were recorded by a Shimazu QP-5050A gas chromatograph–mass spectrometer at the ionizing voltage of 70 eV. The high resolution mass spectra were measured at the Institute for Materials Chemistry and Engineering, Kyushu University, Fukuoka, Japan. The elemental analyses were performed at the Analytical Center of Kumamoto University, Kumamoto, Japan. Manganese(II) acetate tetrahydrate and 2,4-pentanedione were purchased from Wako Pure Chemical Ind., Ltd. Manganese(III) acetate dihydrate, $Mn(OAc)_3\cdot 2H_2O$, was prepared according to the method described in the literature.[10,14] The acetylenes **1** were synthesized according to the literature,[23] except for **1a**, **1j**, and **1k**, which were purchased from Wako Pure Chemical Ind., Ltd: **1b**–**d**,[23a] **1e**,[23b] **1f**–**h**,[23a] **1i**, which were synthesized from 2,4,6-trimethoxybenzaldehyde in a manner similar to that described for the synthesis of 2,6-dibenzyloxy-4-methoxyphenylacetylene,[23c] and **1l**.[23d] 3-Acetyl-1-phenylpentane-1,4-dione (**9**) was prepared by the reaction of 2,4-pentanedione with 2-bromoacetophenone.[14e]

4.2. Manganese(III)-based reaction of arylacetylenes 1a–l with 2,4-pentanedione

An arylacetylene **1** (1 mmol), 2,4-pentanedione (5–12.5 mmol), and glacial acetic acid (30 mL) were placed in a 100 mL round-bottomed flask, and manganese(III) acetate dihydrate (2.5–12.5 mmol) was added. The mixture was stirred at 23 °C in air for 24 h until the arylacetylene **1** was completely consumed, and then the reaction was quenched by adding water (30 mL) to the mixture. The aqueous reaction mixture was extracted with dichloromethane (20 mL×3) and the combined extract was washed with water and then a saturated aqueous solution of sodium hydrogencarbonate. The organic layer was dried over anhydrous magnesium sulfate, filtered, and concentrated in vacuo. The solidified product was filtered to give 1,2-dioxolane **3**. The filtrate was concentrated and the residue was separated by TLC on silica gel (Wakogel B-10) while eluting with diethyl ether/hexane (7:3 v/v) to afford the oxirane **4**. The analytical samples were further purified by recrystallization from the solvent specified in parentheses except for the liquid products. The molar ratios and product yields are summarized in Tables 1 and 2. The specific details are given below.

*4.2.1. 4-Acetyl-5-benzoyl-3-methyl-1,2-dioxolan-3-ol (**3a**)*

Colorless microcrystals (from $CHCl_3$); mp 112–113 °C (lit.[7] mp 145–146 °C); IR (KBr) ν 3650–3200 (OH), 1711, 1695 (C=O); ^{1}H NMR ($CDCl_3$) δ 1.78 (3H, s), 2.39 (3H, s), 3.52 (1H, br), 4.63 (1H, d, J=3.3 Hz), 6.01 (1H, d, J=3.3 Hz), 7.46–8.01 (5H, m); ^{13}C NMR ($CDCl_3$) δ 21.9, 29.9, 69.0, 82.0, 104.8, 128.7, 129.5, 134.0 (2C), 194.7, 201.3. Anal. Calcd for $C_{13}H_{14}O_5$: C, 62.39; H, 5.64. Found: C, 62.18; H, 5.81.

*4.2.2. 4-Acetyl-5-(4-methylbenzoyl)-3-methyl-1,2-dioxolan-3-ol (**3b**)*

Colorless needles (from $CHCl_3$); mp 135 °C; IR (KBr) ν 3650–3200 (OH), 1709, 1693 (C=O); ^{1}H NMR ($CDCl_3$) δ 1.77 (3H, s), 2.39 (3H, s), 2.43 (3H, s), 3.43 (1H, br), 4.62 (1H, d, J=3.3 Hz), 5.97 (1H, d, J=3.3 Hz), 7.25–7.31 (2H, m), 7.86–7.91 (2H, m); ^{13}C NMR ($CDCl_3$) δ 21.8, 21.9, 29.9, 69.1, 82.0, 104.7, 129.4, 129.6, 131.6, 145.1, 194.2, 201.4. Anal. Calcd for $C_{14}H_{16}O_5$: C, 63.63; H, 6.10. Found: C, 63.47; H, 6.21.

*4.2.3. 4-Acetyl-5-(4-methoxybenzoyl)-3-methyl-1,2-dioxolan-3-ol (**3c**)*

Colorless needles (from $CHCl_3$); mp 142 °C; IR (KBr) ν 3650–3200 (OH), 1707, 1686 (C=O); ^{1}H NMR ($CDCl_3$) δ 1.77 (3H, s), 2.39 (3H, s), 3.43 (1H, br), 3.89 (3H, s), 4.65 (1H, d, J=3.3 Hz), 5.95 (1H, d, J=3.3 Hz), 6.93–6.99 (2H, m), 7.95–8.02 (2H, m); ^{13}C NMR ($CDCl_3$) δ 21.9, 30.0, 55.6, 69.0, 82.0, 104.8, 113.9, 127.1, 132.0, 164.2, 192.9, 201.5. Anal. Calcd for $C_{14}H_{16}O_6$: C, 59.99; H, 5.75. Found: C, 59.91; H, 5.82.

*4.2.4. 4-Acetyl-5-(4-chlorobenzoyl)-3-methyl-1,2-dioxolan-3-ol (**3d**)*

Colorless needles (from $CHCl_3$); mp 124–125 °C; IR (KBr) ν 3650–3200 (OH), 1711, 1697 (C=O); ^{1}H NMR ($CDCl_3$) δ 1.77 (3H, s), 2.40 (3H, s), 3.39 (1H, br), 4.63 (1H, d, J=3.1 Hz), 5.95 (1H, d, J=3.1 Hz), 7.44–7.49 (2H, m), 7.92–7.97 (2H, m); ^{13}C NMR ($CDCl_3$) δ 22.0, 29.8, 69.0, 82.2, 104.8, 129.1, 131.0, 132.4, 140.6, 193.8, 201.1. Anal. Calcd for $C_{13}H_{13}ClO_5$: C, 54.84; H, 4.60. Found: C, 54.75; H, 4.68.

*4.2.5. 4-Acetyl-5-(4-fluorobenzoyl)-3-methyl-1,2-dioxolan-3-ol (**3e**)*

Colorless needles (from $CHCl_3$); mp 138 °C; IR (KBr) ν 3650–3200 (OH), 1711, 1697 (C=O); ^{1}H NMR ($CDCl_3$) δ 1.77 (3H, s), 2.40 (3H, s), 3.39 (1H, br), 4.64 (1H, d, J=2.9 Hz), 5.95 (1H, d, J=2.9 Hz), 7.13–7.20 (2H, m), 8.01–8.08 (2H, m); ^{13}C NMR ($CDCl_3$) δ 22.0, 29.8, 69.0, 82.1, 104.8, 115.9 (d, J=22.4 Hz), 130.5 (d, J=2.5 Hz), 132.4 (d, J=9.9 Hz), 166.2 (d, J=256.6 Hz), 193.4, 201.2. Anal. Calcd for $C_{13}H_{13}FO_5$: C, 58.21; H, 4.88. Found: C, 58.13; H, 4.94.

*4.2.6. 4-Acetyl-3-methyl-5-(1-naphthoyl)-1,2-dioxolan-3-ol (**3f**)*

Colorless prisms (from $CHCl_3$); mp 129–130 °C; IR (KBr) ν 3650–3200 (OH), 1699, 1678 (C=O); ^{1}H NMR ($CDCl_3$) δ 1.77 (3H, s), 2.38 (3H, s), 3.67 (1H, br), 4.60 (1H, d, J=2.6 Hz), 6.10 (1H, d, J=2.6 Hz), 7.44–8.58 (7H, m); ^{13}C NMR ($CDCl_3$) δ 22.1, 29.8, 69.9, 83.2, 104.8, 124.2, 125.3, 126.6, 128.3, 128.6, 129.5, 130.8, 132.0, 133.7, 133.9, 199.0, 201.2. Anal. Calcd for $C_{17}H_{16}O_5$: C, 67.99; H, 5.37. Found: C, 67.81; H, 5.28.

*4.2.7. 4-Acetyl-3-methyl-5-(2-naphthoyl)-1,2-dioxolan-3-ol (**3g**)*

Colorless microcrystals (from $CHCl_3$); mp 124–125 °C; IR (KBr) ν 3650–3200 (OH), 1711, 1692 (C=O); ^{1}H NMR ($CDCl_3$) δ 1.79 (3H, s), 2.40 (3H, s), 3.88 (1H, br), 4.69 (1H, d, J=3.3 Hz), 6.18 (1H, d, J=3.3 Hz), 7.48–8.56 (7H, m); ^{13}C NMR ($CDCl_3$) δ 22.0, 29.9, 69.2, 82.1, 104.9, 124.5, 126.9, 127.7, 128.6, 129.0, 129.9, 131.4, 132.1, 132.3, 135.9, 194.7, 201.5. Anal. Calcd for $C_{17}H_{16}O_5$: C, 67.99; H, 5.37. Found: C, 68.14; H, 5.36.

*4.2.8. 4-Acetyl-5-(3,4-dimethoxybenzoyl)-3-methyl-1,2-dioxolan-3-ol (**3h**)*

Colorless microcrystals (from $CHCl_3$); mp 133 °C; IR (KBr) ν 3650–3200 (OH), 1713, 1692 (C=O); ^{1}H NMR ($CDCl_3$) δ 1.78 (3H, s), 2.39 (3H, s), 3.44 (1H, br), 3.94 (3H, s), 3.96 (3H, s), 4.62 (1H, d, J=2.6 Hz), 5.98 (1H, d, J=2.6 Hz), 6.88–6.96 (1H, m), 7.51–7.55 (1H, m), 7.61–7.69 (1H, m); ^{13}C NMR ($CDCl_3$) δ 22.0, 29.9, 56.0, 56.1, 69.3,

81.9, 104.7, 110.1, 111.2, 124.7, 127.1, 149.0, 154.0, 192.9, 201.4. Anal. Calcd for $C_{15}H_{18}O_7 \cdot 1/5H_2O$: C, 57.39; H, 5.91. Found: C, 57.46; H, 5.78. FAB HRMS (acetone/NBA) calcd for $C_{15}H_{18}O_7$ 310.1053 (M). Found 310.0965.

*4.2.9. 2-Acetyl-3-benzoyloxirane (**4a**)*

Colorless microcrystals (from $CHCl_3$/hexane); mp 45–46 °C (lit.[24a] mp 48–49 °C); IR (KBr) ν 1722, 1692 (C=O); ^{1}H NMR ($CDCl_3$) δ 2.23 (3H, s), 3.66 (1H, d, J=1.8 Hz), 4.38 (1H, d, J=1.8 Hz), 7.47–8.03 (5H, m); ^{13}C NMR ($CDCl_3$) δ 25.0, 55.0, 58.7, 128.4, 128.9, 134.4, 134.7, 191.6, 202.9. Anal. Calcd for $C_{11}H_{10}O_3$: C, 69.46; H, 5.30. Found: C, 69.55; H, 5.33.

*4.2.10. 2-Acetyl-3-(4-methylbenzoyl)oxirane (**4b**)*

Colorless microcrystals (from $CHCl_3$/hexane); mp 83 °C; IR (KBr) ν 1711, 1682 (C=O); ^{1}H NMR ($CDCl_3$) δ 2.23 (3H, s), 2.44 (3H, s), 3.66 (1H, d, J=1.8 Hz), 4.34 (1H, d, J=1.8 Hz), 7.28–7.34 (2H, m), 7.87–7.92 (2H, m); ^{13}C NMR ($CDCl_3$) δ 21.8, 25.0, 55.1, 58.8, 128.6, 129.7, 132.4, 145.7, 191.1, 203.0. Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92. Found: C, 70.34; H, 5.74.

*4.2.11. 2-Acetyl-3-(4-methoxybenzoyl)oxirane (**4c**)*

Colorless microcrystals (from $CHCl_3$/hexane); mp 91 °C; IR (KBr) ν 1711, 1680 (C=O); ^{1}H NMR ($CDCl_3$) δ 2.23 (3H, s), 3.66 (1H, d, J=1.8 Hz), 3.90 (3H, s), 4.31 (1H, d, J=1.8 Hz), 6.95–7.01 (2H, m), 7.96–8.03 (2H, m); ^{13}C NMR ($CDCl_3$) δ 25.0, 55.1, 55.6, 58.7, 114.3, 128.0, 131.0, 164.6, 189.8, 203.1. Anal. Calcd for $C_{12}H_{12}O_4$: C, 65.45; H, 5.49. Found: C, 65.47; H, 5.42.

*4.2.12. 2-Acetyl-3-(4-chlorobenzoyl)oxirane (**4d**)*

Colorless microcrystals (from $CHCl_3$/hexane); mp 65–66 °C; IR (KBr) ν 1713, 1690 (C=O); ^{1}H NMR ($CDCl_3$) δ 2.23 (3H, s), 3.66 (1H, d, J=1.8 Hz), 4.29 (1H, d, J=1.8 Hz), 7.47–7.53 (2H, m), 7.92–7.98 (2H, m); ^{13}C NMR ($CDCl_3$) δ 25.0, 55.3, 58.6, 129.4, 129.9, 133.0, 141.2, 190.7, 202.6. Anal. Calcd for $C_{11}H_9ClO_3$: C, 58.81; H, 4.04. Found: C, 58.74; H, 3.86.

*4.2.13. 2-Acetyl-3-(4-fluorobenzoyl)oxirane (**4e**)*

Colorless microcrystals (from $CHCl_3$/hexane); mp 47 °C; IR (KBr) ν 1734, 1682 (C=O); ^{1}H NMR ($CDCl_3$) δ 2.24 (3H, s), 3.66 (1H, d, J=1.8 Hz), 4.32 (1H, d, J=1.8 Hz), 7.15–7.24 (2H, m), 8.01–8.10 (2H, m); ^{13}C NMR ($CDCl_3$) δ 25.0, 55.2, 58.6, 116.3 (d, J=22.4 Hz), 131.2 (d, J=3.1 Hz), 131.3 (d, J=9.3 Hz), 166.4 (d, J=257.8 Hz), 190.2, 202.7. Anal. Calcd for $C_{11}H_9FO_3$: C, 63.46; H, 4.36. Found: C, 63.52; H, 4.24.

*4.2.14. 2-Acetyl-3-(1-naphthoyl)oxirane (**4f**)*

Colorless microcrystals (from $CHCl_3$/hexane); mp 70–71 °C; IR (KBr) ν 1705, 1695 (C=O); ^{1}H NMR ($CDCl_3$) δ 2.20 (3H, s), 3.70 (1H, d, J=1.8 Hz), 4.32 (1H, d, J=1.8 Hz), 7.49–8.60 (7H, m); ^{13}C NMR ($CDCl_3$) δ 24.8, 56.5, 59.0, 124.2, 125.2, 126.9, 128.6 (2C), 129.2, 130.1, 132.0, 133.7, 134.3, 194.5, 203.0. Anal. Calcd for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03. Found: C, 74.88; H, 4.98.

*4.2.15. 2-Acetyl-3-(2-naphthoyl)oxirane (**4g**)*

Colorless microcrystals (from $CHCl_3$/hexane); mp 74 °C; IR (KBr) ν 1715, 1686 (C=O); ^{1}H NMR ($CDCl_3$) δ 2.26 (3H, s), 3.74 (1H, d, J=1.8 Hz), 4.50 (1H, d, J=1.8 Hz), 7.54–8.54 (7H, m); ^{13}C NMR ($CDCl_3$) δ 25.1, 55.1, 58.8, 123.3, 127.1, 127.8, 128.9, 129.3, 129.7, 130.7, 132.1 (2C), 135.9, 191.4, 203.0. Anal. Calcd for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03. Found: C, 75.13; H, 5.02.

*4.2.16. 2-Acetyl-3-(3,4-dimethoxybenzoyl)oxirane (**4h**)*

Colorless prisms (from $CHCl_3$/hexane); mp 109–110 °C; IR (KBr) ν 1711, 1684 (C=O); ^{1}H NMR ($CDCl_3$) δ 2.24 (3H, s), 3.68 (1H, d, J=1.8 Hz), 3.94 (3H, s), 3.98 (3H, s), 4.34 (1H, d, J=1.8 Hz), 6.90–6.95 (1H, m), 7.51–7.55 (1H, m), 7.65–7.70 (1H, m); ^{13}C NMR ($CDCl_3$) δ 25.1, 55.0, 56.1, 56.2, 58.8, 110.2 (2C), 123.6, 128.1, 149.5, 154.6, 189.8, 203.1. Anal. Calcd for $C_{13}H_{14}O_5$: C, 62.39; H, 5.64. Found: C, 62.24; H, 5.60.

*4.2.17. 3-Acetyl-4-hydroxyhex-3-ene-2,5-dione (**6**)*

Colorless prisms (from $CHCl_3$/hexane); mp 115 °C (lit.[10a] mp 115–116 °C); IR (KBr) ν 3400–3000 (OH), 1720, 1654 (C=O); ^{1}H NMR ($CDCl_3$) δ 1.61 (3H, s), 2.40 (3H, s), 2.61 (3H, s), 5.83 (1H, br); ^{13}C NMR ($CDCl_3$) δ 18.8, 21.8, 29.7, 106.1, 113.0, 194.7, 196.9, 197.5. Anal. Calcd for $C_8H_{10}O_4$: C, 56.47; H, 5.92. Found: C, 56.421; H, 6.03.

*4.2.18. 3-Acetyl-2-hydroxy-1-phenylpent-2-ene-1,4-dione (**11**)*

Colorless needles (from $CHCl_3$/hexane); mp 160 °C (lit.[24b] mp 160 °C); IR (KBr) ν 3400–3000 (OH), 1719, 1653 (C=O); ^{1}H NMR ($CDCl_3$) δ 2.39 (3H, s), 2.75 (3H, s), 5.11 (1H, br), 7.39–7.57 (5H, m); ^{13}C NMR ($CDCl_3$) δ 18.6, 29.9, 104.8, 113.1, 125.4, 128.9, 130.2, 134.3, 194.3, 195.6, 197.4. FAB HRMS (acetone/NBA) calcd for $C_{13}H_{13}O_4$ 233.0814 (M+1). Found 233.0802.

*4.2.19. 3-Acetyl-1-(4-methoxyphenyl)pent-2-ene-1,4-dione (**7c**)*[24b]

Yellow oil; IR ($CHCl_3$) ν 1713, 1672, 1600 (C=O); ^{1}H NMR ($CDCl_3$) δ 2.45 (3H, s), 2.46 (3H, s), 3.91 (3H, s), 6.95–7.02 (2H, m), 7.58 (1H, s), 7.94–8.01 (2H, m); ^{13}C NMR ($CDCl_3$) δ 27.4, 30.8, 55.6, 114.3, 129.3, 130.0, 131.2, 151.6, 164.6, 187.8, 196.0, 203.3. FAB HRMS (acetone/NBA) calcd for $C_{14}H_{15}O_4$ 247.0970 (M+1). Found 247.0967.

*4.2.20. 3-Acetyl-1-(3,4-dimethoxyphenyl)pent-2-ene-1,4-dione (**7h**)*

Yellow oil; IR ($CHCl_3$) ν 1705, 1668, 1590 (C=O); ^{1}H NMR ($CDCl_3$) δ 2.45 (3H, s), 2.46 (3H, s), 3.94 (3H, s), 3.98 (3H, s), 6.91–6.95 (1H, m), 7.29 (1H, s), 7.51–7.54 (1H, m), 7.60–7.65 (1H, m); ^{13}C NMR ($CDCl_3$) δ 27.4, 30.8, 56.0, 56.3, 110.1, 110.2, 124.2, 129.6, 129.8, 149.7, 151.6, 154.6, 187.8, 196.0, 203.2. FAB HRMS (acetone/NBA) calcd for $C_{15}H_{17}O_5$ 277.1076 (M+1). Found 277.1045.

*4.2.21. 3-Acetyl-1-(2,4,6-trimethoxyphenyl)pent-2-ene-1,4-dione (**7i**)*

Yellow oil; IR ($CHCl_3$) ν 1705, 1670, 1607 (C=O); ^{1}H NMR ($CDCl_3$) δ 2.38 (6H, s), 3.83 (6H, s), 3.86 (3H, s), 6.12 (2H, s), 7.14 (1H, s); ^{13}C NMR ($CDCl_3$) δ 27.1, 30.8, 55.6, 56.1, 90.7, 110.9, 136.0, 148.1, 160.8, 164.5, 189.6, 197.2, 203.4. FAB HRMS (acetone/NBA) calcd for $C_{16}H_{19}O_6$ 307.1182 (M+1). Found 307.1181.

*4.2.22. (E)-1-(2,4,6-Trimethoxyphenyl)pent-2-ene-1,4-dione (**8i**)*

Yellow needles (from $CHCl_3$/hexane); mp 74–75 °C; IR ($CHCl_3$) ν 1668, 1605 (C=O); ^{1}H NMR ($CDCl_3$) δ 2.37 (3H, s), 3.78 (6H, s), 3.85 (3H, s), 6.12 (2H, s), 6.71 (1H, d, J=16.1 Hz), 7.10 (1H, d, J=16.1 Hz); ^{13}C NMR ($CDCl_3$) δ 28.1, 55.5, 55.9, 90.7, 110.7, 137.0, 140.2, 159.6, 163.5, 193.0, 199.3. FAB HRMS (acetone/NBA) calcd for $C_{14}H_{17}O_5$ 265.1076 (M+1). Found 265.1061.

4.3. Manganese(III)-mediated aerobic oxidation of 1,4-pentanedione 9

A solution of the 1,4-pentanedione **9** (1 mmol) and manganese(III) acetate dihydrate (0.1 mmol) in glacial acetic acid (15 mL) was stirred at 23 °C in air for 12 h until the 1,4-pentanedione **9** was completely consumed, and then the reaction was quenched by adding water (15 mL) to the mixture. The aqueous reaction mixture was extracted with dichloromethane (10 mL×3) and the combined extract was first washed with water and then a saturated aqueous solution of sodium hydrogencarbonate. The organic layer was dried over anhydrous magnesium sulfate, filtered, and then concentrated to dryness. The products were separated by flash column chromatography on silica gel (Silica Gel 60N, 40–50 μm, Kanto Chemical Co., Inc.), while eluting with diethyl

ether/hexane (7:3 v/v) to afford 3-hydroxy-1-phenylpent-2-ene-1,4-dione (**10**). The product **10** was further purified by recrystallization from chloroform/hexane.

*4.3.1. 3-Hydroxy-1-phenylpent-2-ene-1,4-dione (**10**)*

Colorless microcrystals (from $CHCl_3$/hexane); mp 95–96 °C; IR (KBr) ν 3400–3000 (OH), 1674, 1590 (C=O); ^{1}H NMR ($CDCl_3$) δ 2.50 (3H, s), 6.94 (1H, s), 7.44–8.03 (5H, m), 15.37 (1H, br); ^{13}C NMR ($CDCl_3$) δ 25.1, 93.8, 127.8, 128.9, 133.7, 135.2, 173.6, 190.8, 197.6. FAB HRMS (acetone/NBA) calcd for $C_{11}H_{11}O_3$ 191.0708 (M+1). Found 191.0749.

4.4. Silica gel-mediated decomposition reaction of 1,2-dioxolanes 3a–h

To a solution of a 1,2-dioxolane **3** (0.1 mmol) in methanol (10 mL) was added silica gel (Wakogel B-10, 0.5 g), and the mixture was stirred at room temperature for 12 h. Dichloromethane (10 mL) was added to the resulting suspension, which was filtered under reduced pressure. The reaction flask and the silica gel were washed well with dichloromethane/methanol (9:1 v/v), and the combined filtrates were concentrated in vacuo. The residue was suspended again with dichloromethane (5 mL), and filtered through a cotton plug. The filtrate was concentrated in vacuo to give the oxirane **4**.

Acknowledgements

This research was supported by Grants-in-Aid for Scientific Research (C), No. 15550039 and No. 19550046, from the Japan Society for the Promotion of Science. We gratefully acknowledge Professor Teruo Shinmyozu, Institute for Materials Chemistry and Engineering, Kyushu University, Japan, for measurement of the high resolution FAB mass spectrum.

Supplementary data

Copies of ^{1}H NMR, ^{13}C NMR, and IR spectra for new compounds **3a–h**, **4a–h**, **7h**, **7i**, **8i**, and **10** (100 pages). Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.02.045.

References and notes

1. (a) Casteel, D. A. *Nat. Prod. Rep.* **1992**, *9*, 289–312; (b) Casteel, D. A. *Nat. Prod. Rep.* **1999**, *16*, 55–73.
2. Nicolaou, K. C.; Gacic, G. P.; Barnette, W. E. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 293–312.
3. (a) Haynes, R. Y.; Vonwiller, S. C. *Acc. Chem. Res.* **1997**, *30*, 73–79; (b) Mekonnen, B.; Ziffer, H. *Tetrahedron Lett.* **1997**, *38*, 731–734; (c) Posner, G. H.; O'Dowd, H.; Caferro, T.; Cumming, J. N.; Ploypradith, P.; Xie, S.; Shapiro, T. A. *Tetrahedron Lett.* **1998**, *39*, 2273–2276; (d) Provt, O.; Camuzat-Dedenis, B.; Hamzaoui, M.; Moskowitz, H.; Mayrargue, J.; Robert, A.; Cazelles, J.; Meunier, B.; Zouhiri, F.; Desmaële, D.; D'Angelo, J.; Mahuteau, J.; Gay, F.; Cicéron, L. *Eur. J. Org. Chem.* **1999**, 1935–1938; (e) Borstnik, K.; Paik, I.; Shapiro, T. A.; Posner, G. H. *Int. J. Parasitol.* **2002**, *32*, 1661–1667; (f) Robert, A.; Dechy-Cabaret, O.; Cazelles, J.; Meunier, B. *Acc. Chem. Res.* **2002**, *35*, 167–174; (g) Haynes, R.; Ho, W.-Y.; Chan, H.-W.; Fugmann, B.; Stetter, J.; Croft, S. L.; Vivas, L.; Peters, W.; Robinson, B. L. *Angew. Chem., Int. Ed.* **2004**, *43*, 1381–1385; (h) Posner, G. H.; O'Neill, P. M. *Acc. Chem. Res.* **2004**, *37*, 397–404; (i) Bachi, M. D.; Korshin, E. E.; Hoos, R.; Szpilman, A. M.; Ploypradith, P.; Xie, S.; Shapiro, T. A.; Posner, G. H. *J. Med. Chem.* **2003**, *46*, 2516–2533; (j) Tang, Y.; Dong, Y.; Vennerstrom, J. L. *Med. Res. Rev.* **2004**, *24*, 425–448.
4. Pillipson, D. W.; Rinehart, K. L. *J. Am. Chem. Soc.* **1983**, *105*, 7735–7736.
5. Davidson, B. S. *J. Org. Chem.* **1991**, *56*, 6722–6724.
6. Nishino, H. In *Bioactive Heterocycles I*; Eguchi, S., Ed.; Springer: Berlin, 2006; pp 39–76 and references cited therein.
7. Qian, C.-Y.; Han, B.; Zhao, Y. F.; Noiri, Y.; Nishino, H.; Kurosawa, K. *Chin. Chem. Lett.* **1997**, *8*, 189–190.
8. (a) Blood, A. J.; Bothwell, B. D.; Collins, A. N.; Maidwell, N. L. *Tetrahedron Lett.* **1996**, *37*, 1885–1888; (b) Bloodworth, A. J.; Curtius, R. J.; Spencer, M. D.; Tallant, N. A. *Tetrahedron* **1993**, *49*, 2729–2750; (c) Carless, H. A. S.; Batten, R. J. *J. Chem. Soc., Perkin Trans. 1* **1987**, 1999–2007; (d) O'Connor, D. E.; Mihelich, E. D.; Coleman, M. C. *J. Am. Chem. Soc.* **1984**, *106*, 3577–3584; (e) Barker, P. J.; Beckwith, A. L. J.; Fung, Y. *Tetrahedron Lett.* **1983**, *24*, 97–100; (f) Cativiela, C.; Figueras, F.; Fraile, J. M.; Garcîa, J. I.; Mayoral, J. A. *Tetrahedron Lett.* **1995**, *36*, 4125–4128; (g) Hernández, R.; Velázquez, S. M.; Suárez, E. *Tetrahedron Lett.* **1996**, *37*, 6409–6412; (h) Feldman, K. S. *Synlett* **1995**, 217–225; (i) Ensley, H. E.; Carr, R. V. C.; Martin, R. S.; Pierce, T. E. *J. Am. Chem. Soc.* **1980**, *102*, 2836–2838; (j) Dussault, P. H.; Zope, U. R. *Tetrahedron Lett.* **1995**, *36*, 2187–2190; (k) Keul, H.; Choi, H.-S.; Kuczkowski, R. L. *J. Org. Chem.* **1985**, *50*, 3365–3371; (l) Casey, M.; Culshaw, A. J. *Synlett* **1992**, 214–216; (m) Bunnelle, W. H. *Chem. Rev.* **1991**, *91*, 335–362; (n) Dussault, P. H.; Zope, U. R. *Tetrahedron Lett.* **1995**, *36*, 3655–3658; (o) Ramirez, A.; Woerpel, K. A. *Org. Lett.* **2005**, *7*, 4617–4620; (p) Baumstark, A. L.; Vasquez, P. C. *J. Org. Chem.* **1992**, *57*, 393–395; (q) Tokuyasu, T.; Kunikawa, S.; McCullough, K. J.; Masuyama, A.; Nojima, M. *J. Org. Chem.* **2005**, *70*, 251–260; (r) Dai, P.; Dussault, P. H. *Org. Lett.* **2005**, *7*, 4333–4335; (s) Oku, A.; Yokoyama, T.; Harada, T. *Tetrahedron Lett.* **1983**, *24*, 4699–4702; (t) Morisson, V.; Barnier, J.-P.; Blanco, L. *Tetrahedron Lett.* **1999**, *40*, 4045–4046; (u) Kulinkovich, O. G.; Astashko, D. A.; Tyvorskii, V. I.; Ilyina, N. A. *Synthesis* **2001**, 1453–1455; (v) Tokuyasu, T.; Kunikawa, S.; Masuyama, A.; Nojima, M. *Org. Lett.* **2002**, *4*, 3595–3598; (w) Kirihara, M.; Kakuda, H.; Ichinose, M.; Ochiai, Y.; Takizawa, S.; Mokuya, A.; Okubo, K.; Hatano, A.; Shiro, M. *Tetrahedron* **2005**, *61*, 4831–4839; (x) Wimalasena, K.; Wickman, H. B.; Mahindaratne, M. P. D. *Eur. J. Org. Chem.* **2001**, 3811–3817; (y) Madelaine, C.; Six, Y.; Buriez, O. *Angew. Chem., Int. Ed.* **2007**, *46*, 8046–8049.
9. (a) Citterio, A.; Sebastino, R.; Carvayal, M. C. *J. Org. Chem.* **1991**, *56*, 5335–5341; (b) Citterio, A.; Sebastino, R.; Maronati, A.; Saniti, R.; Bergamini, F. *J. Chem. Soc., Chem. Commun.* **1994**, 1517–1518; (c) Nguyen, V.-H.; Nishino, H.; Kajikawa, S.; Kurosawa, K. *Tetrahedron* **1998**, *54*, 11445–11460; (d) Montevencchi, P. C.; Navacchia, M. L. *Tetrahedron* **2000**, *56*, 9339–9342; (e) Yilmaz, M.; Pekel, A. T. *Synth. Commun.* **2001**, *31*, 3871–3876; (f) Bar, G.; Parsons, A. F.; Thomas, C. B. *Tetrahedron* **2001**, *57*, 4719–4728; (g) Melikyan, G. G.; Sargsyan, A. B.; Giri, V. S.; Grigoryan, R. T.; Badanyan, Sh. O. *Chem. Heterocycl. Compd.* **1988**, *24*, 258–263; (h) Melikyan, G. G.; Sargsyan, A. B.; Badanyan, Sh. O. *Chem. Heterocycl. Compd.* **1989**, *25*, 606–609; (i) Cossy, J.; Leblanc, C. *Tetrahedron Lett.* **1989**, *30*, 4531–4534; (j) Oumar-Mahamat, H.; Surzur, M. J.-M.; Bertrand, M. P. *J. Org. Chem.* **1989**, *54*, 5684–5688; (k) Snider, B. B.; Zhang, Q.; Dombroski, M. A. *J. Org. Chem.* **1992**, *57*, 4195–4205; (l) Snider, B. B.; McCarthy, B. A. *J. Org. Chem.* **1993**, *58*, 6217–6223; (m) Okuro, K.; Alper, H. *J. Org. Chem.* **1996**, *61*, 5312–5315; (n) Brocksom, T. J.; Coelho, F.; Deprés, J.-P.; Greene, A. E.; Freire de Lima, M. E.; Hamelin, O.; Hartmann, B.; Kanazawa, A. M.; Wang, Y. *J. Am. Chem. Soc.* **2002**, *124*, 15313–15325; (o) Sung, K.; Wang, Y. Y. *J. Org. Chem.* **2003**, *68*, 2771–2778.
10. (a) Nishino, H. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 1733–1739; (b) Nishino, H.; Tategami, S.; Yamada, T.; Korp, J. D.; Kurosawa, K. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 1800–1809.
11. Snider, B. B.; Merritt, J. E.; Dombroski, M. A.; Buckman, B. O. *J. Org. Chem.* **1991**, *56*, 5544–5553.
12. Ionization potential of acetylene: 11.4 eV (calcd 11.6 eV); phenylacetylene **1a**: (calcd 9.4 eV); ethene: 10.5 eV (calcd 10.6 eV); styrene: 8.5 eV (calcd 9.2 eV); 1,1-diphenylethene: (calcd 9.1 eV). The ionization potential was referred to Kimura, K.; Katsumata, S.; Achiba, Y.; Yamazaki, T.; Iwata, S. *Handbook of Hel Photoelectron Spectra of Fundamental Organic Molecules*; Japan Scientific Societies: Tokyo, 1981; and was also calculated by CAChe version 4.9.3.
13. (a) Saniti, R.; Bergamini, F.; Citterio, A.; Sebastino, R.; Nicolini, M. *J. Org. Chem.* **1992**, *57*, 4250–4255; (b) Alagoz, O.; Yilmaz, M.; Pekel, A. T. *Synth. Commun.* **2006**, *36*, 1005–1013; (c) Lee, Y. R.; Byun, M. W.; Kim, B. S. *Bull. Korean Chem. Soc.* **1998**, *19*, 1080–1083; (d) Melikyan, G. G. *Org. React.* **1997**, *49*, 427–675 and references cited therein.
14. (a) Yamada, T.; Iwahara, Y.; Nishino, H.; Kurosawa, K. *J. Chem. Soc., Perkin Trans. 1* **1993**, 609–616; (b) Nishino, H.; Nguyen, V.-H.; Yoshinaga, S.; Kurosawa, K. *J. Org. Chem.* **1996**, *61*, 8264–8271; (c) Nguyen, V.-H.; Nishino, H.; Kurosawa, K. *Synthesis* **1997**, 899–908; (d) Nguyen, V.-H.; Nishino, H.; Kurosawa, K. *Heterocycles* **1998**, *48*, 465–480; (e) Chowdhury, F. A.; Nishino, H.; Kurosawa, K. *Heterocycles* **1999**, *51*, 575–591; (f) Nguyen, V.-H.; Nishino, H. *Tetrahedron Lett.* **2004**, *45*, 3373–3377; (g) Asahi, K.; Nishino, H. *Tetrahedron* **2005**, *61*, 11107–11124; (h) Asahi, K.; Nishino, H. *Tetrahedron Lett.* **2006**, *47*, 7259–7262; (i) Asahi, K.; Nishino, H. *Tetrahedron* **2008**, *64*, 1620–1634; (j) Asahi, K.; Nishino, H. *Eur. J. Org. Chem.* **2008**, 2401–2416.
15. Kasai, P. H.; McBay, H. C. *J. Phys. Chem.* **1984**, *88*, 5932–5934.
16. (a) Benati, L.; Montevecchi, P. C.; Spagnolo, P. *J. Chem. Soc., Perkin Trans. 1* **1991**, 2103–2109; (b) Kopping, B.; Chatgilialoglu, C.; Zehnder, M.; Giese, B. *J. Org. Chem.* **1992**, *57*, 3994–4000; (c) Metzger, J. O.; Blumenstein, M. L. *Chem. Ber.* **1993**, *126*, 2493–2499; (d) Benati, L.; Capella, L.; Montevecchi, P. C.; Spagnolo, P. *J. Chem. Soc., Perkin Trans. 1* **1995**, 1035–1038; (e) Huang, X.; Liang, C.-G.; Xu, Q.; He, Q.-W. *J. Org. Chem.* **2001**, *66*, 74–80.
17. The rate constant of trapping of the unsubstituted vinyl radical is 10^9 M^{-1} s^{-1} order, see: (a) Park, J.-Y.; Heaven, M. C.; Gutman, D. *Chem. Phys. Lett.* **1984**, *104*, 469–474; (b) Slagle, I. R.; Park, J.-Y.; Heaven, M. C.; Gutman, D. *J. Am. Chem. Soc.* **1984**, *106*, 4356–4361; (c) Krueger, H.; Weitz, E. *J. Chem. Phys.* **1988**, *88*, 1608–1616; (d) Fahr, A.; Laufer, A. H. *J. Phys. Chem.* **1988**, *92*, 7229–7232; (e) Knyazev, V. D.; Slagle, I. R. *J. Phys. Chem.* **1995**, *99*, 2247–2249; (f) Eskola, A. J.; Timonen, R. S. *Phys. Chem. Chem. Phys.* **2003**, *5*, 2557–2561; For other carbon-centered radicals, see: (g) Maillard, B.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 5095–5099 and references cited therein.
18. (a) Carpenter, B. K. *J. Phys. Chem.* **1995**, *99*, 9801–9810; (b) Yang, R.; Yu, L.; Jin, X.; Zhou, M.; Carpenter, B. K. *J. Chem. Phys.* **2005**, *122*, 014511.
19. (a) Sheldon, R. A.; Kochi, J. K. *Metal Catalyzed Oxidations of Organic Compounds*; Academic: New York, NY, 1981; For examples of the decomposition by Fe ions, see: (b) Sato, T.; Oikawa, T.; Kobayashi, K. *J. Org. Chem.* **1985**, *50*, 1646–1651; (c)

Sun, M.; Deng, Y.; Batyreva, E.; Sha, W.; Salomon, R. G. *J. Org. Chem.* **2002**, *67*, 3575–3584; (d) Masuyama, A.; Sugawara, T.; Nojima, M.; McCullough, K. J. *Tetrahedron* **2003**, *59*, 353–366; For Co ions, see: (e) Sakaguchi, S.; Kato, S.; Iwahama, T.; Ishii, Y. *Bull. Chem. Soc. Jpn.* **1998**, 1237–1240; (f) Iwahama, T.; Sakaguchi, S.; Ishii, Y. *Chem. Commun.* **2000**, 613–614; (g) Hirao, K.; Sakaguchi, S.; Ishii, Y. *Tetrahedron Lett.* **2002**, *43*, 3617–3620; For Mn ions, see: (h) Rahman, M. T.; Nishino, H. *Org. Lett.* **2003**, *5*, 2887–2890.

20. (a) Porter, N. A. In *Organic Peroxides*; Ando, W., Ed.; Wiley: New York, NY, 1992, Chapter 2; (b) Arends, I. W. C. E.; Ingold, K. U.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1995**, *117*, 4710–4711; (c) Kim, J.; Harrison, R. G.; Kim, C.; Que, L., Jr. *J. Am. Chem. Soc.* **1996**, *118*, 4373–4379.
21. 3-Acetyl-2-hydroxy-1-phenylpent-2-ene-1,4-dione (**11**) (2%) was also isolated in the reaction (Table 1, entry 24). If we venture a guess, the pentenedione **11** might be formed by the oxidative decomposition of the dihydrodioxinal **A**.
22. Barnier, J.-P.; Morisson, V.; Blanco, L. *Synth. Commun.* **2001**, *31*, 349–357.
23. (a) Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* **1972**, *36*, 3769–3772; (b) Lambert, J. B.; Larson, E. G.; Bosch, R. J.; TeVrucht, M. L. E. *J. Am. Chem. Soc.* **1985**, *107*, 5443–5447; (c) Li, C. C.; Xie, Z. X.; Zhang, Y. D.; Chen, J. H.; Yang, Z. *J. Org. Chem.* **2003**, *68*, 8500–8504; (d) Torrado, A.; López, S.; Alvarez, R.; de Lera, A. R. *Synthesis* **1995**, 285–293.
24. (a) Chien, C.-S.; Kawasaki, T.; Sakamoto, M.; Tamura, Y.; Kita, Y. *Chem. Pharm. Bull.* **1985**, *33*, 2743–2749; (b) Onitsuka, S.; Nishino, H.; Kurosawa, K. *Tetrahedron* **2001**, *57*, 6003–6009.