FORMATION OF ENDOPEROXIDES FROM Mn(III)-INDUCED REACTION OF 1,1-DIARYLETHENE, DIKETENE AND ETHANOL

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Abstract

Diketene reacted with manganese(III) acetate dihydrate in the presence of ethanol as a nucleophile to give a mixture of nonconjugated manganese(III) enolate **A** and conjugated manganese(III) enolate **B**. Major 1,2-dioxan-3-ol products **2** and **4** were formed by the oxidation of unstable nonconjugated manganese(III) enolate **A**. The proportions of **2** and **4** depended on the amount of diketene used. 1,2-Dioxan-3-ol **3** derived from the conjugated manganese(III) enolate **B** was also obtained as a minor product. The reaction pathways are briefly discussed.

Keywords. Endoperoxides, aerobic oxidation, manganese(III) acetate, diketene, alkenes.

1. INTRODUCTION

Manganese(III) acetate is well known as a mild one-electron oxidant that leads to dicarbonylmethyl radical, ·CH(COR)COR', from 1,3-dicarbonyl compounds. Hence, the manganese(III)-induced reaction of alkenes and 1,3-dicarbonyl compounds has been, and continues to be, a simple and convenient method for the synthesis of heterocycles containing one oxygen atom, especially the five-membered ring ones [2]. We have had a longstanding interest in this area and in the previous report we described the formation of tetrahydrofuran derivatives using carbon radicals derived from manganese(III) oxidation of diketene [3]. Since manganese(III)-induced molecular oxygen trapping reactions have been extensively investigated [4], it seemed reasonable to anticipate the formation of 1,2-dioxan-3-ols in a similar reaction of alkenes with diketene in the presence of a nucleophile. With this in mind, we checked the oxidation of diketene with manganese(III) acetate dehydrate ($Mn(OAc)_3$·$2H_2O$) in the presence of a 1,1-diarylethene and ethanol.

2. EXPERIMENTAL SECTION

2.1. Measurements

All of the ^{1}H and ^{13}C NMR spectra were recorded with a JNM PMX-60SI or a JNM EX-90 FT NMR spectrometer at 60 or 90 MHz for ^{1}H and 22.5 MHz for ^{13}C, respectively, with tetramethylsilane as the internal standard. The chemical shifts are shown in δ values (ppm). The IR spectra were measured on a JASCO A-102 IR spectrometer and the IR spectral data are expressed in cm^{-1}. Mass spectra were measured on either a SHIMADZU GCMS QP5000 or a JMS-LX1000 mass spectrometer. Elemental analyses were performed at the Elemental analyses Center of Kyushu University, Fukuoka, Japan. All of the melting points were determined with a Yanaco micromelting-point apparatus MP-J3 and were uncorrected.

2.2. Materials

Manganese(III) acetate dihydrate, $Mn(OAc)_3$·$2H_2O$, was prepared according to the literature method [5]. 1,1-Diarylethenes **1a-c** were prepared by dehydration of the corresponding alcohols, which were synthesized from substituted acetophenones and arylmagnesium bromides [6]. Manganese(II) acetate tetrahydrate, diketene, ethanol and glacial acetic acid were purchased from Wako Pure Chemical Ind., Ltd., and were used as received.

2.3. Reaction procedure

1,1-Diarylethene (1 mmol) was weighed into a 50 mL flask equipped with a magnetic stirrer. Glacial acetic acid (10 mL), diketene (1.5-4 mmol),

manganese (III) acetate dihydrate (4 mmol) and ethanol (200 mmol) were added and the mixture was stirred at 23 °C under air for the period of time mentioned in tables 1 and 2. The solvent was removed *in vacuo*, and the residue was quenched with water. The aqueous mixture was extracted with chloroform. The extract was concentrated to dryness, and the products were separated on silica gel TLC (Wakogel B-10 or Merck Kieselgel 60 F$_{254}$) with diethyl ether/*n*-hexane (3:7 v/v) as the developing solvent. Solid products were further recrystallized by indicated solvent. The ^{1}H NMR spectra of **2a** showed two adjacent methylene groups as multiplet at 1.66-3.02 ppm which was assigned to –CH$_2$CH$_2$– moiety of dioxan ring. The hydroxylic proton gave a broad singlet at 5.56 ppm and was confirmed by its disappearance when added to the sample tube one drop of D$_2$O. The ^{13}C NMR spectrum of this product showed a quaternary ^{13}C peak at 98.83 ppm which was characteristic for C-3 of 1,2-dioxan-3-ols [4]. Specific details are given below.

2.4. Product data

3-(Ethoxycarbonyl)methyl-6,6-diphenyl-1,2-dioxan-3-ol (2a): colorless needles (from petroleum ether/ *n*-hexane); mp 93-93.5 °C; IR (CHCl$_3$) ν 3600 (OH), 1717 (CO); ^{1}H NMR (CDCl$_3$, δ, ppm) 1.23 (3H, t, *J* = 7 Hz, –OCH$_2$CH$_3$), 1.66-3.02 (4H, m, –CH$_2$CH$_2$–), 2.56 (2H, s, –CH$_2$CO$_2$Et), 4.15 (2H, q, *J* = 7 Hz, –OCH$_2$CH$_3$), 5.56 (1H, br s, OH), 7.16-7.70 (10H, m, arom H); ^{13}C NMR (CDCl$_3$, δ, ppm) 170.85 (C=O), 143.40, 142.06 (arom C), 128.44, 128.27, 127.68, 126.81, 126.17 (arom CH), 98.83 (O–C–O), 85.36 (C–O), 61.27 (CH$_2$O), 41.19, 29.98, 29.03 (CH$_2$), and 14.01 (CH$_3$). Anal. calcd for C$_{20}$H$_{22}$O$_5$: C, 70.15; H, 6.47. Found: C, 70.24; H, 6.46.

6,6-Bis(4-chlorophenyl)-3-(ethoxycarbonyl)methyl-1,2-dioxan-3-ol (2b): yellowish liquid; IR (CHCl$_3$) ν 3600 (OH), 1720 (CO); ^{1}H NMR (CDCl$_3$, δ, ppm) 1.23 (3H, t, *J* = 7 Hz, –OCH$_2$CH$_3$), 1.66-3.02 (4H, m, –CH$_2$CH$_2$–), 2.56 (2H, s, –CH$_2$CO$_2$Et), 4.23 (2H, q, *J* = 7 Hz, –OCH$_2$CH$_3$), 5.71 (1H, br s, OH), and 7.31-7.51 (8H, m, arom H).

3-(Ethoxycarbonyl)methyl-6,6-bis(4-methylphenyl)-1,2-dioxan-3-ol (2c): colorless liquid; IR (CHCl$_3$) ν 3600 (OH), 1720 (CO); ^{1}H NMR (CDCl$_3$, δ, ppm) 1.23 (3H, t, *J* = 7 Hz, –OCH$_2$CH$_3$), 1.60-2.86 (4H, m, –CH$_2$CH$_2$–), 2.26 (3H, s, CH$_3$), 2.33 (3H, s, CH$_3$), 2.56 (2H, s, –CH$_2$CO$_2$Et), 4.18 (2H, q, *J* = 7 Hz, –OCH$_2$CH$_3$),

54.83 (1H, br s, OH), 7.03-7.53 (8H, m, arom H); FAB MS (positive ion) *m/z*, 353 (M$^+$+OH, 4), 245 (16), 221 (14), 189 (17), 171 (34), 165 (27), 129 (37), 119 (93), 105 (25), 91 (100), and 77 (21).

4-Ethoxycarbonyl-3-methyl-6,6-diphenyl-1,2-dioxan-3-ol (3a): colorless microcrystals (from petroleum ether/ *n*-hexane); mp 150-150.5 °C; IR (CHCl$_3$) ν 3600 (OH), 1727 (CO); ^{1}H NMR (CDCl$_3$, δ, ppm) 1.28 (3H, t, *J* = 7 Hz, –OCH$_2$CH$_3$), 1.40 (3H, s, CH$_3$), 2.86 (3H, m, –CHCH$_2$–), 4.23 (2H, q, *J* = 7 Hz, –OCH$_2$CH$_3$), 7.30-7.66 (10H, m, arom H). Anal. calcd for C$_{20}$H$_{22}$O$_5$: C, 70.15; H, 6.47. Found: C, 70.17; H, 6.41.

6,6-Bis(4-chloro)phenyl-4-ethoxycarbonyl-3-methyl-1,2-dioxan-3-ol (3b): colorless plates (from petroleum ether/*n*-hexane); mp 144-145 °C; IR (CHCl$_3$) ν 3600 (OH), 1727 (CO); ^{1}H NMR (CDCl$_3$, δ, ppm) 1.28 (3H, t, *J* = 7 Hz, –OCH$_2$CH$_3$), 1.40 (3H, s, CH$_3$), 2.81 (3H, m, –CHCH$_2$–), 4.23 (2H, q, *J* = 7 Hz, –OCH$_2$CH$_3$), 3.86 (1H, br s, OH), 7.26-7.53 (8H, m, arom H). Anal. calcd for C$_{20}$H$_{20}$O$_5$Cl$_2$: C, 58.41; H, 4.90. Found: C, 58.36; H, 4.91.

4-Ethoxycarbonyl-6,6-bis(4-methylphenyl)-3-methyl-1,2-dioxan-3-ol (3c): colorless prisms (from petroleum ether/*n*-hexane); mp 151-151.5 °C; IR (CHCl$_3$) ν 3588 (OH), 1728 (CO); ^{1}H NMR (CDCl$_3$, δ, ppm) 1.28 (3H, t, *J* = 7 Hz, –OCH$_2$CH$_3$), 1.40 (3H, s, CH$_3$), 2.33 (6H, s, 2xCH$_3$), 2.86 (3H, m, –CHCH$_2$–), 4.23 (2H, q, *J* = 7 Hz, –OCH$_2$CH$_3$), 7.03-7.56 (8H, m, arom H). Anal. calcd for C$_{20}$H$_{26}$O$_5$: C, 71.33; H, 7.07. Found: C, 71.29; H, 7.11.

4-Ethoxycarbonyl-3-hydroxymethyl-6,6-diphenyl-1,2-dioxan-3-ol (4a): colorless microcrystals (from petroleum ether/ *n*-hexane); mp 113-114 °C; IR (CHCl$_3$) ν 3600, 3550 (OH), 1732 (CO); ^{1}H NMR (CDCl$_3$, δ, ppm) 1.26 (3H, t, *J* = 7 Hz, –OCH$_2$CH$_3$), 2.56-3.02 (3H, m, –CHCH$_2$–), 3.64 (1H, d, *J* = 12.2 Hz, H^a–CHOH), 3.77 (1H, d, *J* = 12.2 Hz, H^b–CHOH), 4.17 (2H, q, *J* = 7 Hz, –OCH$_2$CH$_3$), 7.07-7.58 (10H, m, arom H); ^{13}C NMR (CDCl$_3$, δ, ppm) 171.42 (C=O), 143.21, 140.64 (arom C), 128.54, 128.33, 128.06, 127.52, 126.82, 126.02 (arom CH), 99.14 (O–C–O), 85.69 (C–O), 65.02, 61.55 (CH$_2$O), 41.50 (CH), 31.45 (CH$_2$), and 14.07 (CH$_3$). Anal. calcd for C$_{20}$H$_{22}$O$_6$: C, 67.02; H, 6.18. Found: C, 67.26; H, 6.10.

6,6-Bis(4-chlorophenyl)-4-ethoxycarbonyl-3-hydroxymethyl-1,2-dioxan-3-ol (4b): colorless liquid; IR (CHCl$_3$) ν 3620, 3540 (OH), 1730 (CO); ^{1}H NMR (CDCl$_3$, δ, ppm) 1.23 (3H, t, *J* = 7 Hz, –OCH$_2$CH$_3$), 2.88 (3H, m, –CHCH$_2$–), 3.51 (1H, d, *J* = 12 Hz, H$_a$–CHOH), 3.86 (1H, d, *J* = 12 Hz, H$_b$–CHOH), 4.23 (2H, q, *J* = 7 Hz, –OCH$_2$CH$_3$), and 7.26-7.55 (8H, m, arom H).

4-Ethoxycarbonyl-3-hydroxymethyl-6,6-bis(4-methylphenyl)-1,2-dioxan-3-ol (4c): colorless liquid; IR (CHCl$_3$) ν 3600, 3540 (OH), 1730 (CO); ^{1}H NMR (CDCl$_3$, δ, ppm) 1.28 (3H, t, J = 7 Hz, –OCH$_2$CH$_3$), 2.28 (3H, s, CH$_3$), 2.35 (3H, s, CH$_3$), 2.92 (3H, m, –CHCH$_2$–), 3.53 (1H, d, J = 12 Hz, H^a–CHOH), 3.83 (1H, d, J = 12 Hz, H^b–CHOH), 4.21 (2H, q, J = 7 Hz, –OCH$_2$CH$_3$), 7.03-7.61 (8H, m, arom H); FAB MS (positive ion) *m/z*, 387 (M$^+$+OH, 4), 239 (11), 202 (32), 189 (32), 178 (41), 165 (41), 128 (59), 91 (100), 77 (39), and 55 (54).

Benzophenone (5a): colorless prisms (from diethyl ether/*n*-hexane); mp 46-47 ^{o}C; IR (CHCl$_3$) ν 1660 (CO); ^{1}H NMR (CDCl$_3$, δ, ppm) 7.30-8.12 (m, arom) [7].

4,4'-Dichlorobenzophenone (5b): colorless prisms (from diethyl ether/*n*-hexane); mp 150-150.5 ^{o}C; IR (CHCl$_3$) ν 1660 (CO); ^{1}H NMR (CDCl$_3$, δ, ppm) 6.95-7.95 (m, arom) [8].

4,4'-Dimethylbenzophenone (5c): colorless microcrystals (from diethyl ether/*n*-hexane); mp 93.5-94.5 ^{o}C; IR (CHCl$_3$) ν 1650 (CO); ^{1}H NMR (CDCl$_3$, δ, ppm) 2.51 (6H, s, 2 x CH$_3$), 7.30-7.91 (m, arom) [3].

2-(Ethoxycarbonyl)methyl-3-ethoxy-5,5-bis(4-methylphenyl)tetrahydrofuran (6c): colorless liquid; IR (CHCl$_3$) ν 1735 (CO); ^{1}H NMR (CDCl$_3$, δ, ppm) 0.91 (3H, t, J = 7 Hz, –OCH$_2$CH$_3$), 1.21 (3H, t, J = 7.1 Hz, –CO$_2$CH$_2$CH$_3$), 2.02-2.91 (4H, m, –CH$_2$CH$_2$–), 2.28 (6H, s, 2 x CH$_3$), 2.63 (1H, d, J = 13.7 Hz, H^a–CHCO$_2$Et), 3.19 (1H, d, J = 13.7 Hz, H^b–CHCO$_2$Et), 3.58 (2H, q, J = 7 Hz, –OCH$_2$CH$_3$), 4.13 (2H, q, J = 7.1 Hz, –CO$_2$CH$_2$CH$_3$), 7.10-7.32 (8H, m, arom H); ^{13}C NMR (CDCl$_3$, δ, ppm) 169.60 (C=O), 144.18, 143.83, 136.09 (arom C), 128.70, 128.64, 128.60, 126.64, 125.93, 125.42 (arom CH),

107.14 (O–C–O), 89.34 (C–O), 60.43, 66.91 (CH$_2$O), 42.16, 37.75, 37.18 (CH$_2$), 20.95, 20.91, 15.10, and 14.13 (CH$_3$); MS *m/z* (rel intensity), 382 (M$^+$, 29), 337 (65), 320 (25), 291 (42), 245 (100), 221 (77), 211 (55), 182 (35), 172 (82), 143 (59), 129 (43), 119 (69), 105 (22), 91 (34), and 43 (23).

2-Ethoxycarbonyl-5,5-bis(4-methylphenyl)-2-methyltetrahydrofuran (7c): colorless liquid; ^{1}H NMR (CDCl$_3$, δ, ppm) 0.92 (3H, t, J = 7 Hz, –OCH$_2$CH$_3$), 1.56 (3H, s, –CH$_3$), 1.73-2.96 (4H, m, –CH$_2$CH$_2$–), 2.30 (6H, s, 2 x CH$_3$), 3.56 (2H, q, J = 7 Hz, –OCH$_2$CH$_3$), 7.03-7.50 (8H, m, arom H); MS *m/z* (rel intensity), 310 (M$^+$, 3), 295 (3), 265 (13), 219 (27), 129 (14), 100 (60), 72 (55), 57 (18), and 43 (100).

3. RESULTS AND DISCUSSION

3.1. Oxidation of a mixture of 1,1-diphenylethene and diketene in the presence of ethanol

Reaction of 1,1-diphenylethene (**1a**), diketene, ethanol and Mn(OAc)$_3$·2H$_2$O in glacial acetic acid at 23 ^{o}C for 36 h afforded 1,2-dioxan-3-ols **2a** (18 %), **3a** (9 %) and **4a** (7 %) together with 21 % yield of benzophenone (scheme 1 and table 1, Entry 1). The isolation of **2a** is significant, in that, to our knowledge, there are no earlier reports on the manganese(III)-induced formation of 1,2-dioxan-3-ol derivatives which contain no substituent at the 4-position. When a similar mixture was allowed to react for 30 h, the yield of **2a** was improved to 26% yield (table 1, Entry 2). However, a further shortened reaction time resulted in a worse yield of this product (table 1, Entry 3). Decreasing amount of Mn(OAc)$_3$·2H$_2$O favored the formation of **4a** (table 1, Entry 4).
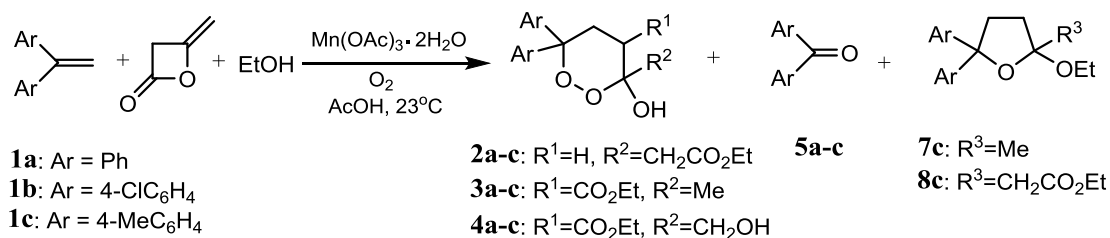
Table 1: Manganese(III) oxidation of a mixture of 1,1-diarylethenes **1a-c** and diketene in the presence of ethanol[a]

Entry	Ethene	Molar ratio[b]	Time (h)	Product (yield %)[c]				
1	**1a**	1:1.5:4:200	16	**2a** (15)	**3a** (5)	**4a** (22)	**5a** (16)	
2	**1a**	1:4:4:200	20	**2a** (16)	**3a** (5)	**4a** (9)	**5a** (18)	
3	**1a**	1:4:4:200	30	**2a** (26)	**3a** (7)	**4a** (7)	**5a** (21)	
4	**1a**	1:4:4:200	36	**2a** (18)	**3a** (9)	**4a** (7)	**5a** (21)	
5	**1b**	1:4:4:200	30	**2b** (15)	**3b** (3)	**4b** (5)	**5b** (15)	
6	**1b**	1:1.5:4:200	16	**2b** (15)	**3b** (4)	**4b** (20)	**5b** (14)	
7	**1c**	1:4:4:200	20	**2c** (30)	**3c** (9)	**4c** (6)	**5c** (9)	**6c** (6) **7c** (3)
8	**1c**	1:1.5:4:200	12	**2c** (38)	**3c** (9)	**4c** (12)	**5c** (8)	**6c** (2) **7c** (2)

[a] The reaction was caried out in glacial acetic acid (10 mL) at room temperature.

[b] Diarylethene (1 mmol):diketene:Mn(OAc)$_3$·2H$_2$O:ethanol.

[c] Isolated yield based on the amount of the diarylethene used.

Scheme 1: Reaction of 1,1-diarylethene **1a-c** with diketene and ethanol in the presence of manganese triacetate dehydrate

2.2. Oxidation of a mixture of 1,1-diarylethene and diketene in the presence of ethanol

In an attempt to investigate the effect of a substituent on benzene ring, 1,1-bis(4-chlorophenyl)ethene (**1b**) and 1,1-bis(4-methylphenyl)ethene (**1c**) were used. A similar oxidation of **1b** gave **2b**, **3b**, **4b** and **5b**. The presence of a methyl group at the 4-position of benzene ring preferentially provided product **2** (Table 2, Entry 7 and 8). It was noteworthy that in the reaction of **1c**, two tetrahydrofuran derivatives (**6c** and **7c**) were also formed in small amounts (table 1, Entries 7 and 8).

2.3. Reaction pathways

The mechanism for the formation of radicals by a manganese(III) acetate-mediated oxidation system was well-documented by Fristad [9a] and Snider [2,9b]. Being similar to a mechanism outlined in our previous report [3, 4] in this present reaction, the corresponding nonconjugated enolate **A** would be directly formed by the attack of ethanol on the carbonyl carbon of diketene in the manganese(III) coordination atmosphere (scheme 2). The enolate **A** could be expected to be easily converted to conjugated enolate **B**, since the conjugated enolate **B** is more stable than nonconjugated enolate **A**. These enolates would react with the alkene employed to form the obtained products by a radical pathways described in the literatures [10, 11]. It is interesting that the total yield of the 1,2-dioxan-3-ols derived from the enolate **A**, i.e. **2** and **4**, is much higher than that of the 1,2-dioxan-3-ol derivatives from **B**, i.e. **3** (Table 1), although the conjugated enolate complex **B** is more stable than the nonconjugated enolate complex **A**. If it is supposed that the rates of all reactions from **A** and **B** are the same, the reaction of diketene, ethanol and manganese(III) acetate would be kinetically controlled under the giving reaction conditions. Namely, the formation of **A** and **B** is determined by relatively rates of competing reactions rather than by the relative stabilities of these two complexes.
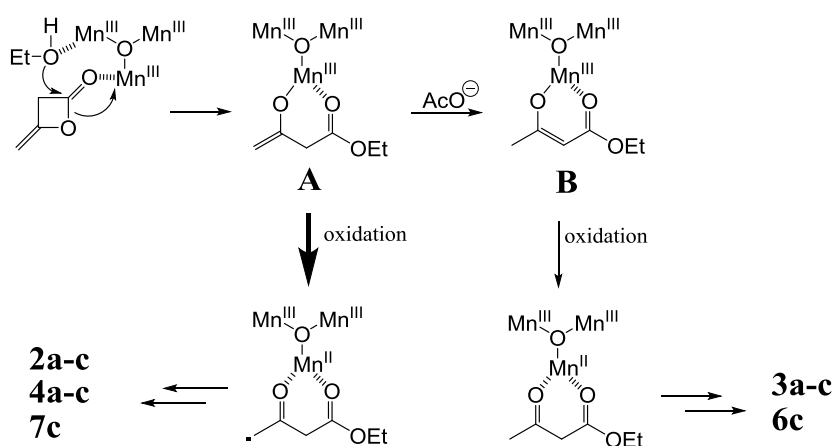
Scheme 2: Proposed mechanism for the formation of products

4. CONCLUSION

We examined the molecular oxygen trapping reaction of 1,1-diarylethenes with diketene and ethanol in the presence of manganese(III) acetate dihydrate and elucidated the reaction pathways for the formation of 1,2-dioxan-3-ol products. Although the moderate yields of these products presented a

potential drawback with this reaction, the proportions of products proved that the preferential reaction would take place *via* the unstable nonconjugated enolate.

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