Title

Formation of 1,2-Dioxan-3-ol Derivatives from Manganese(III)-Based Oxidative Reaction Using Diaryl…

Author(s)

Van-Ha, Nguyen; Hiroshi, Nishino

Citation

熊本大学極低温装置室ユーザー研究報告書 : 熊大極低温, 20: 5-9

Issue date

2010-03

Type

Departmental Bulletin Paper

URL

http://hdl.handle.net/2298/27686
Formation of 1,2-Dioxan-3-ol Derivatives from Manganese(III)-Based Oxidative Reaction Using Diarylethenes, Diketene, and Ethanol

Van-Ha Nguyen\textsuperscript{a} and Hiroshi Nishino\textsuperscript{b}\textsuperscript{*}

\textsuperscript{a}Department of Chemistry, Dalat University, 1 Phu Dong Thien Vuong St., Dalat, Vietnam
\textsuperscript{b}Department of Chemistry, Graduate School of Science and Technology, Kumamoto University, Kurokami 2-39-1, Kumamoto 860-8555, Japan

Abstract: Diketene readily underwent reaction with manganese(III) acetate dihydrate in the presence of ethanol as a nucleophile to produce the enolate complexes A and B, of which subsequent reaction with diarylethenes 1 in air gave three 1,2-dioxan-3-ol products 2, 3, and 4. Major products 2 and 4 were produced by the oxidation of unstable nonconjugated manganese(III)-enolate complex A. The proportion of 2 and 4 depended on the amount of diketene used. The 1,2-dioxan-3-ol 3 derived from the conjugated manganese(III)-enolate complex B was also obtained as a minor product. The reaction pathway for the formation of the endoperoxides 2-4 is discussed.

Keywords: Endoperoxides; Aerobic oxidation; Manganese(III) acetate; Diketene; Kinetic control

Introduction

Heterocycles containing 1,2-dioxane ring system are present in many natural products and some have been shown to possess various biological activities.\textsuperscript{1} We have paid our attention to use manganese(III)-based reactions to produce heterocycles and found that the synthetic methodology could be applied well for the preparation of a variety of 1,2-dioxan-3-ol derivatives.\textsuperscript{2} We previously described the formation of tetrahydrofuran derivatives using carbon radicals derived from manganese(III) oxidation of diketene at elevated temperature.\textsuperscript{3} In systematically extending our earlier studies, it became worth to examine a similar reaction using 1,1-diarylethenes, diketene, and ethanol at room temperature in air. In this communication, we report the results of the reaction and briefly discuss the reaction pathway.

Results and Discussion

Oxidation of a Mixture of 1,1-Diarylethenes and Diketene with Manganese(III) Acetate Dihydrate in the Presence of Ethanol.

The results of our experiments are presented in Scheme 1 and Table 1. In an initial experiment, the reaction of a mixture of 1,1-diphenylethene (1\textsubscript{a}), diketene, and ethanol with manganese(III) acetate dihydrate gave 1,2-dioxan-3-ols \textsubscript{2a} (15\%), \textsubscript{3a} (5\%), and \textsubscript{4a} (22\%) together with a 16\% yield of benzophenone (5\textsubscript{a}) (Entry 1). The structure of these products was determined by spectroscopic methods.\textsuperscript{4} This result showed, reasonably enough, the preferential reaction took place via the less stable nonconjugated enolate A. The isolation of \textsubscript{2a} is significant, in that, as far as we know, this is the first report of the manganese(III)-induced formation of 1,2-dioxan-3-ol derivative which contains no substituent at the 4-position. Prolongation of the reaction time did not improve the product yield (Entry 4). The use of a slight excess amount of diketene favored the production of \textsubscript{4a} (Entry 1), while the reaction using four equivalents of diketene preferred the formation of \textsubscript{2a} except for that of benzophenone (5\textsubscript{a}) (Entry 3).
Scheme 1

Table 1. Manganese(III) Oxidation of a Mixture of 1,1-Diarylethenes 1a-c and Diketene in the Presence of Ethanol

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ethene</th>
<th>Molar ratio $^b$</th>
<th>Time (h)</th>
<th>Product (yield %)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2a (15)</td>
</tr>
<tr>
<td>1</td>
<td>1a</td>
<td>1:1.5:4:200</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1a</td>
<td>1:4:4:200</td>
<td>20</td>
<td>2a (16)</td>
</tr>
<tr>
<td>3</td>
<td>1a</td>
<td>1:4:4:200</td>
<td>30</td>
<td>2a (26)</td>
</tr>
<tr>
<td>4</td>
<td>1a</td>
<td>1:4:4:200</td>
<td>36</td>
<td>2a (18)</td>
</tr>
<tr>
<td>5</td>
<td>1b</td>
<td>1:4:4:200</td>
<td>30</td>
<td>2b (15)</td>
</tr>
<tr>
<td>6</td>
<td>1b</td>
<td>1:1.5:4:200</td>
<td>16</td>
<td>2b (15)</td>
</tr>
<tr>
<td>7</td>
<td>1c</td>
<td>1:4:4:200</td>
<td>20</td>
<td>2c (30)</td>
</tr>
<tr>
<td>8</td>
<td>1c</td>
<td>1:1.5:4:200</td>
<td>12</td>
<td>2c (38)</td>
</tr>
</tbody>
</table>

$^a$ The reaction was carried out in glacial acetic acid (10 mL) at room temperature.

$^b$ Diarylethene (1 mmol): diketene:Mn(OAc)$_2$:2H$_2$O:ethanol.

$^c$ Isolated yield based on the amount of the diarylethene used.
A similar reaction of 1,1-bis(4-chlorophenyl)ethene (1b) and 1,1-bis(4-methylphenyl)ethene (1c) gave similar products (Entries 5-8). In the case of 1c, a small amount of two tetrahydrofurans 6c and 7c was also produced (Entries 7, 8). Clearly, the product distribution depended on the nature of the substituent on the phenyl group of 1. The introduction of an electron-releasing group such as methyl group resulted in the formation of 2 over 4 (Entries 7, 8), whereas an electron-withdrawing group such as chlorine preferentially provided 4 (Entry 6).

**Reaction Pathway.**

The formation of 1,2-dioxan-3-ols 2, 3, and 4 could be explained by the sequence depicted in Scheme 2. In the first step, the addition of ethanol to diketene in the manganese(III) coordination atmosphere in a similar manner described in the literature would produce the enolate complex A. The enolate complex A could be expected to be easily converted into the conjugated enolate complex B. In the presence of diarylethene 1, the radicals E and F must be formed from the enolates A and B, respectively. The former should be produced via an α-keto radical C. On the other hand, an electron donor-acceptor-like complex D would be an intermediate for the formation of the latter.
In an alternative pathway, the manganese(III) oxidation of the radical C would result in the formation of alcohol G which could be easily converted into the corresponding manganese(III)-enolate complex H in the oxidation system. It should be noted that, although containing a hydroxyl group at the terminal carbon, the complex H is quite similar to the enolate B. Therefore, a D-like complex and an F-like radical could be also expected to be formed from the enolate H by a similar process in which the complex D and the radical F would be produced from the enolate B. The formed radicals, namely the radicals E, F, and the F-like radical in the case of the enolate H, could then be trapped by dissolved molecular oxygen to afford the corresponding peroxy radicals which would be reduced by manganese(II) and subsequently cyclized to give the 1,2-dioxan-3-ol 2, 3, and 4, respectively.2,8

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. This suggests that the proportion of the alternative products 2, 3, and 4 is determined by the relative rate of the formation. That is, the enolate complex A would be produced under kinetic control.

The by-product tetrahydrofuran 6c would be produced by the reaction of 1c with the conjugated enolate complex B followed by further oxidative decarboxylation and then attack of ethanol instead of molecular oxygen.3 The tetrahydrofuran carboxylate 7c would also be obtained by the reaction of 1c with the nonconjugated enolate complex A followed by further oxidation and subsequent attack of ethanol.3 The other by-product benzophenone (5a) was produced by direct oxidation of 1a with manganese(III) acetate dihydrate.2e

Conclusion

In summary, we scrutinized the formation of 1,2-dioxan-3-ol derivatives using carbon radicals derived from the manganese(III) oxidation of diketene. Although the moderate yields of the products presented as a potential drawback in this reaction, the proportion of the products proved that the preferential reaction would take place via the formation of the unstable nonconjugated enolate complex such as A.

Acknowledgment

We are very grateful to Professor Emeritus Kazu Kurosawa, Kumamoto University, Japan for his helpful discussion. This research was supported by Grants-in-Aid for Scientific Research (C), No.08640691, No. 15550039, and No.19550046, from the Japan Society for the Promotion of Science.

References


4. The reaction was carried out as follows. A mixture of alkene 1 (1 mmol), diketene (1.5-4 mmol), manganese(III) acetate dihydrate (4 mmol), and ethanol (200 mmol) was stirred in glacial acetic acid (10 mL) at 23 °C under air for the period of time mentioned in Table 1. The solvent was removed in vacuo and the residue was triturated with water followed by extraction with chloroform. The extract was washed with a saturated aqueous solution of sodium hydrogen carbonate and concentrated to dryness. The products were separated by silica gel TLC (Wakogel B-10) with diethyl ether-hexane (3:7 v/v) as the developing solvent. The crystalline products were recrystallized from appropriate solvent (vide infra).

Selected spectroscopic data as follows.

2a: Colorless needles (from petroleum ether/ hexane); mp 93-93.5 °C; IR (CHCl₃) ν 3600, 1717; ¹H NMR (CDCl₃) δ 1.23 (3H, t, J = 7 Hz), 1.66-3.02 (4H, m), 2.56 (2H, s), 4.15 (2H, q, J = 7 Hz), 5.56 (1H, br s), 7.16-7.70 (10H, m); ¹³C NMR (CDCl₃) δ 170.9, 143.4, 142.1, 128.4, 128.3, 127.7, 126.8, 126.2, 98.8, 85.4, 61.3, 41.2, 30.0, 29.0, and 14.0. Anal. calcd for C₂₀H₂₂O₅: C, 70.15; H, 6.47. Found: C, 70.24; H, 6.46.

3a: Colorless microcrystals (from petroleum ether/ hexane); mp 150-150.5 °C; IR (CHCl₃) ν 3600, 1727; ¹H NMR (CDCl₃) δ 1.28 (3H, t, J = 7 Hz), 1.40 (3H, s), 2.86 (3H, m), 4.23 (2H, q, J = 7 Hz), 7.30-7.66 (10H, m). Anal. calcd for C₂₀H₂₂O₅: C, 70.15; H, 6.47. Found: C, 70.17; H, 6.41.

4a: Colorless microcrystals (from petroleum ether/ hexane); mp 113-114 °C; IR (CHCl₃) ν 3600, 3550, 1732; ¹H NMR (CDCl₃) δ 1.26 (3H, t, J = 7 Hz), 2.56-3.02 (3H, m), 3.64 (1H, d, J = 12.2 Hz), 3.77 (1H, d, J = 12.2 Hz), 4.17 (2H, q, J = 7 Hz), 7.07-7.58 (10H, m); ¹³C NMR (CDCl₃) δ 171.4, 143.2, 140.6, 128.5, 128.3, 128.1, 127.5, 126.8, 126.0, 99.1, 85.7, 65.0, 61.6, 41.5, 31.5, and 14.1. Anal. calcd for C₂₀H₂₂O₆: C, 67.02; H, 6.18. Found: C, 67.26; H, 6.10.


