The reactions of acylferrocenes with samarium diiodide: reduction, deoxygenation, reductive coupling and rearrangement

Shean-Jeng Jong a,b, Jim-Min Fang a,*, Chun-Hsu Lin b

a Department of Chemistry, National Taiwan University, Taipei, 106 Taiwan, ROC
b Chemical System Research Division, Chung-Shan Institute of Science and Technology, PO Box 90008-17, Lung Tan, Taiwan, ROC

Received 1 June 1999; received in revised form 9 July 1999

Abstract

Acylferrocenes reacted with samarium diiodide in the presence of water to give the corresponding (α-hydroxyalkyl)ferrocenes or alkylferrocenes depending on the reaction time and temperature. On treatment with samarium diiodide in the absence of water, ferrocenecarbaldehyde underwent a reductive coupling to give pinacols, whereas acetylferrocene yielded 3,3-diferrocenyl-2-butanone and 2,3-diferrocenyl-2-butene via the subsequent rearrangement and deoxygenation. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Acylferrocenes; Samarium diiodide; Reduction; Deoxygenation; Pinacol; Rearrangement

1. Introduction

SmI2 is a one-electron-transfer reducing agent [1], which is widely utilized to react with various functional groups. Since samarium ion is oxophilic, the reactions of SmI2 with carbonyl groups are very efficient. The generated ketyl radical anion can abstract a hydrogen atom to give alcohols, or couple with the second molecule of carbonyls to give pinacols. Such reductions and reductive couplings of aromatic carbonyl compounds have been reported [2]. Except for the property of one-electron redox [3], acylferrocenes are known to exhibit the reaction aptitude similar to aromatic carbonyl compounds in many aspects. For example, reductions of acylferrocenes are generally carried out by using NaBH4 or LiAlH4 to give the corresponding (α-hydroxyalkyl)ferrocenes [4]. Acylferrocenes are subjected to catalytic hydrogenation to afford the corresponding alkylferrocenes [5]. Such deoxygenations are also achieved by using combined reagents [6] including Na/EtOH, Zn(Hg) + HCl (Clemmensen reduction), LiAlH4 + AlCl3, NaBH4 + ZnCl2, NaBH3CN + BF3, NaBH4CN + TiCl4 and Et3SiH + TiCl4. The study of the reactions of acylferrocenes with SmI2 is so far elusive. As acylferrocenes are readily available precursors viable to derivatization for the preparation of catalysts and materials [7], their reactivity towards SmI2 is worthwhile to investigate.

2. Results and discussion

Table 1 lists the results of the reactions of acylferrocenes 1a–c and 2 with SmI2 in THF solution. In the presence of H2O (11 equiv.), the reaction of ferrocenecarbaldehyde (1a) with SmI2 (2.6 equiv.) at 0°C for a short period (10 min) gave exclusively ferrocenemethanol (3a) in 93% yield (Eq. (1)). When 1a was treated with SmI2 (8 equiv.) and water (20 equiv.) in refluxing THF for a prolonged period (4 h), a deoxygenation product 4a was obtained. In similar ways (entries 2 and 4), acetylferrocene (1b) was either reduced at 0°C to give the alcohol 3b (92%) or deoxygenated at 68°C to give 4b (85%). Use of less SmI2/H2O (entry 5) resulted in a decreased yield (61%) of 4b. Deoxygenation of benzoylferrocene (Eq. (1)) and 1,1-diacylferrocene (Eq. (2)) was also successfully carried out to give benzylferrocene (4c) and 1,1-diethylferrocene (5), respectively. Such deoxygenations could result from the subsequent reduction of the intermediate...
Table 1  
The reactions of acylferrocenes 1a-c and 2 with SmI₂ in THF solution

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>SmI₂/substrate molar ratio</th>
<th>Additive</th>
<th>Reaction temp./°C</th>
<th>Reaction time</th>
<th>Products (yield %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1a</td>
<td>2.6</td>
<td>H₂O (11 equiv.)</td>
<td>25</td>
<td>10 min</td>
<td>3a (93)</td>
</tr>
<tr>
<td>2</td>
<td>1b</td>
<td>2.6</td>
<td>H₂O (11 equiv.)</td>
<td>25</td>
<td>10 min</td>
<td>3b (92)</td>
</tr>
<tr>
<td>3</td>
<td>1a</td>
<td>8</td>
<td>H₂O (20 equiv.)</td>
<td>68</td>
<td>4 h</td>
<td>4a (70)</td>
</tr>
<tr>
<td>4</td>
<td>1b</td>
<td>8</td>
<td>H₂O (20 equiv.)</td>
<td>68</td>
<td>24 h</td>
<td>4b (85)</td>
</tr>
<tr>
<td>5</td>
<td>1b</td>
<td>4</td>
<td>H₂O (8 equiv.)</td>
<td>68</td>
<td>4 h</td>
<td>4b (61)</td>
</tr>
<tr>
<td>6</td>
<td>1c</td>
<td>8</td>
<td>H₂O (20 equiv.)</td>
<td>68</td>
<td>16 h</td>
<td>4c (44)</td>
</tr>
<tr>
<td>7</td>
<td>2</td>
<td>16</td>
<td>H₂O (40 equiv.)</td>
<td>68</td>
<td>16 h</td>
<td>5 (67)</td>
</tr>
<tr>
<td>8</td>
<td>1a</td>
<td>8</td>
<td>None</td>
<td>68</td>
<td>48 h</td>
<td>6 (42)*</td>
</tr>
<tr>
<td>9</td>
<td>1b</td>
<td>8</td>
<td>None</td>
<td>68</td>
<td>48 h</td>
<td>7 (20) + 8 (43)*</td>
</tr>
<tr>
<td>10</td>
<td>1b</td>
<td>8</td>
<td>Sieves (200 mg)</td>
<td>68</td>
<td>48 h</td>
<td>7 (25) + 8 (56)*</td>
</tr>
<tr>
<td>11</td>
<td>1b</td>
<td>8</td>
<td>HMPA (0.6 equiv.)</td>
<td>68</td>
<td>48 h</td>
<td>7 (23) + 8 (36)*</td>
</tr>
<tr>
<td>12</td>
<td>1b</td>
<td>8</td>
<td>HMPA (1.4 equiv.)</td>
<td>68</td>
<td>48 h</td>
<td>7 (18) + 8 (51)*</td>
</tr>
</tbody>
</table>

* Compound 6 existed as a mixture of stereomers (1:1), and compound 8 existed as a mixture of geometric isomers in predominance of the Z-isomer (63–86%).

ferrocenyl alcohols with an excess of SmI₂, and these processes might be facilitated by the in situ generated Sm(III) ion of Lewis acid nature. Indeed, 1-ferroceny lethanol (3b) reacted with SmI₂: H₂O in refluxing THF gave ethylferrocene (4b), the anticipated deoxygenation product, in a quantitative yield.

In the absence of H₂O, ferrocenecarbaldehyde underwent a reductive coupling to give the pinacol 6 (Eq. (3)), whereas acetylferrocene yielded 3,3-diferrocenyl-2-butanone (7) and 2,3-diferrocenyl-2-butene (8) on treatment with SmI₂ in refluxing THF (Eq. (4)). The diol 6 existed as a mixture of two stereomers in equal amounts, whereas the alkene 8 existed as a mixture of geometric isomers with a predominance of the Z-isomer (63–86%). The configuration of isomers was determined by analysis of their ¹H NMR spectra. The signals of Z-8 occurred at higher fields than the corresponding resonances of E-isomer. A previously reported reaction [8] of acetylferrocene with Zn/TiCl₄ gives 8 with an E/Z ratio of 3. The Z/E selectivity might be attributable to the kinetic control of individual reducing agent in the reductive olefination. By comparison of entry 9 with entries 10–12, the yields and Z/E ratio were slightly changed when acetylferrocene was treated with SmI₂ in the presence of molecular sieves or hexamethylphosphoramide.

The pinacol 6 was unstable; it was easily oxidized to ferrocenecarbaldehyde (the parent aldehyde 1a) on standing. Compounds 7 and 8 could result from the same intermediate of the putative pinacol A (or the corresponding samarium pinacolate), which might rearrange subsequently to give the ketone 7 or react further with SmI₂ to give the alkene 8 (Eq. (4)). The pinacol A was previously found in the reaction of acetylferrocene with electrochemically generated sodium amalgam [9], but not with magnesium amalgam [10]. The pinacol A can be oxidized, back to acetylferrocene on exposure to the air [4b,9]. Treatment of A with HClO₄ results in a rearrangement to give the butanone 7 [4b,9].
3. Experimental

3.1. General methods

Melting points are uncorrected. Chemical shifts are reported relative to CHCl$_3$ $[\delta_H$ 7.26, $\delta_C$ (central line of t) 77.0]. All reactions requiring anhydrous conditions were conducted in flame-dried apparatus under an atmosphere of nitrogen. Syringes and needles for the transfer of reagents were dried at 120°C and allowed to cool in a desiccator over P$_2$O$_5$ before use. THF was distilled from sodium benzophenone ketyl.

3.2. Representative procedure for reduction of acylferrocenes

A deep blue SmI$_2$ solution (0.1 M, 1.8 mmol) was prepared by treatment of Sm (330 mg, 2.2 mmol) with 1,2-dioiodoethane (500 mg, 1.8 mmol) in anhydrous THF (18 ml) for 1.5 h at room temperature (r.t.). After addition of H$_2$O (135 mg, 7.5 mmol), the mixture was heated under reflux for 50 min, cooled, and filtered through a pad of silica gel by elution with EtOAc. Further purification by silica gel column (3:97 EtOAc–hexane) afforded 4a (140 mg, 70%).

3.2.1. Ferrocenymethanol [4b], 3a

According to the representative procedure (Section 3.2), ferrocenecarbaldehyde (150 mg, 0.7 mmol) was treated with SmI$_2$ in THF at 0°C for 10 min to give 3a (141 mg, 93%). $^1$H-NMR (CDCl$_3$, 200 MHz) $\delta$ 4.30 (2 H, s), 4.21 (2 H, m), 4.15 (5 H, s), 4.14 (2 H, m), 1.89 (1 H, s). $^{13}$C-NMR (CDCl$_3$, 50 MHz) $\delta$ 60.6, 67.9 (2 C), 68.2 (7 C), 88.1.

3.2.2. 1-Ferroceylethanol [4a], 3b

$^1$H-NMR (CDCl$_3$, 300 MHz) $\delta$ 4.56 (1 H, q, $J = 6.3$ Hz), 4.17–4.06 (9 H, m), 2.19 (1 H, s), 1.41 (3 H, d, $J = 6.3$ Hz). $^{13}$C-NMR (CDCl$_3$, 50 MHz) $\delta$ 23.5, 65.3, 65.8, 66.1, 67.6, 67.7, 68.1 (5 C), 94.3.

3.3. Representative procedure for deoxygenation of acylferrocenes

A deep blue SmI$_2$ solution (0.11 M, 8.0 mmol) was prepared by treatment of Sm (1.20 g, 8.0 mmol) with 1,2-dioiodoethane (2.25 g, 8.0 mmol) in anhydrous THF (70 ml) for 1.5 h at r.t. After addition of H$_2$O (360 mg, 20 mmol), a solution of 1a (214 mg, 1.0 mmol) in THF (10 ml) was added in one portion. The mixture was heated under reflux for 4 h. The serum cap was removed, and hexane (20 ml) was added. The resulting precipitates were removed by passing through a pad of silica gel, and the crude product was obtained by elution with EtOAc. Further purification by silica gel column (3:97 EtOAc–hexane) afforded 4a (140 mg, 70%).

3.3.1. Methylferrocene [6f], 4a

$^{13}$C-NMR (CDCl$_3$, 50 MHz) $\delta$ 14.8, 67.1 (2 C), 68.5 (5 C), 69.1 (2 C), 83.9. Anal. Calc. for C$_{11}$H$_{12}$Fe: C, 66.04; H, 6.05. Found: C, 65.85; H, 6.12.

3.3.2. Ethylferrocene [6f], 4b

According to the representative procedure (Section 3.3), acetylferrocene (228 mg, 1 mmol) was treated with SmI$_2$ in refluxing THF for 48 h to give 4b (182 mg, 85%) after chromatography on a silica gel column (3:97 EtOAc–hexane).

Compound 4b was also prepared from the alcohol 3b by the following procedure. A mixture of 3b (230 mg, 1 mmol) and water (98 mg, 5.5 mmol) in THF (10 ml) was added to a THF solution (40 ml) of SmI$_2$ (3.6 mmol). The mixture was heated under reflux for 50 min, cooled, and filtered through a pad of silica gel by elution with EtOAc–hexane (1:1) to give a practically pure sample of 4b (211 mg, 99%) as shown by $^1$H- and $^{13}$C-NMR analyses. $^{13}$C-NMR (CDCl$_3$, 50 MHz) $\delta$ 14.6, 22.2, 66.8 (2 C), 67.4 (2 C), 68.3 (5 C), 91.0. Anal. Calc. for C$_{12}$H$_{14}$Fe: C, 67.30; H, 6.59. Found: C, 67.05; H, 6.50.

3.3.3. Benzylferrocene [6f], 4c

According to the representative procedure (Section 3.3), benzylferrocene (290 mg, 1 mmol) was treated with SmI$_2$ in refluxing THF for 16 h to give 4c (122 mg, 44%) after chromatography on a silica gel column (3:97 EtOAc–hexane). $^{13}$C-NMR (CDCl$_3$, 50 MHz) $\delta$ 36.0, 67.5 (2 C), 68.6 (7 C), 87.9, 125.8, 128.2 (2 C), 128.3 (2 C), 141.5. FAB-MS $m/z$ 276 (M$^+$).

3.3.4. 1,1′-Diethylferrocene [6f], 5

According to the representative procedure (Section 3.3), 1,1′-diacetylferrocene (270 mg, 1 mmol) was treated with SmI$_2$ in refluxing THF for 16 h to give 5 (162 mg, 67%) after chromatography on a silica gel column by elution with hexane and EtOAc–hexane (3:97). $^{13}$C-NMR (CDCl$_3$, 50 MHz) $\delta$ 15.4 (2 C), 22.7 (2 C), 68.1 (4 C), 68.5 (4 C), 91.6 (2 C). FAB-MS $m/z$ 242 (M$^+$).

3.4. 1,2-Diferrocenyl-1,2-ethanediol [11], 6

Ferrocenecarbaldehyde (214 mg, 1 mmol) was treated with SmI$_2$ (8 mmol) in anhydrous THF under reflux for 48 h. After addition of ice water (50 ml), the mixture was extracted with CHCl$_3$ (30 ml $\times$ 10). The extracts were combined, washed with water, concentrated, and crystallized from MeOH–H$_2$O to give the pinacols 6 (90 mg, 42%) as a mixture of two stereomers (1:1). $^1$H-
NMR (CDCl₃, 200 MHz) δ 2.24/2.51 (2 H, s, OH), 3.88/4.06 (4 H, m), 4.12/4.22 (4 H, m), 4.17 (10 H, s), 4.24/4.30 (2 H, s). FAB-MS m/z 430 (M⁺).

3.5. The reaction of acetylferrocene with SmI₂ in the absence of water.

Acetylferrocene (228 mg, 1 mmol) was treated with SmI₂ (8 mmol) in anhydrous THF under reflux for 48 h. Hexane was added, and the resulting precipitates were removed by passing through a pad of silica gel. The filtrate was concentrated and chromatographed on a silica gel column by elution with hexane and EtOAc–hexane (5:95) to give the ketone 7 (44 mg, 20%) and the alkene 8 (71 mg, 43%).

3.5.1. 3,3-Diferrocenyl-2-butanone [9], 7

1H-NMR (CDCl₃, 200 MHz) δ 1.86 (3 H, s), 2.04 (3 H, s), 4.06 (4 H, m), 4.08 (10 H, s), 4.16 (4 H, m). 13C-NMR (CDCl₃, 50 MHz) δ 24.1, 27.6, 50.7, 66.8, 67.0, 67.7, 67.8, 68.8 (4 C), 93.5 (2 C), 207.2. FAB-MS m/z 440 (M⁺).

3.5.2. 2,3-Diferrocenyl-2-butene [8], 8

1H-NMR (CDCl₃, 200 MHz, Z-isomer) δ 2.11 (6 H, s), 3.88 (4 H, m), 4.02 (4 H, m), 4.05 (10 H, s); 1H-NMR (CDCl₃, 200 MHz, E-isomer) δ 2.15 (6 H, s), 4.15 (10 H, s), 4.22 (4 H, m), 4.31 (4 H, m). FAB-MS m/z 424 (M⁺). Anal. Calc. for C₃₄H₂₄Fe₂: C, 67.96; H, 5.70. Found: C, 67.67; H, 5.60.

Acknowledgements

We thank the National Science Council of the Republic of China for financial support (NSC 88-2113-M-002-023).

References