

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

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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.

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1. Introduction

SmI_2 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 SmI_2 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 NaBH_4 or LiAlH_4 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 , $\text{Zn(Hg)} + \text{HCl}$ (Clemmensen reduction), $\text{LiAlH}_4 + \text{AlCl}_3$, $\text{NaBH}_4 + \text{ZnCl}_2$, $\text{NaBH}_3\text{CN} + \text{BF}_3$, $\text{NaBH}_3\text{CN} + \text{TiCl}_4$ and $\text{Et}_3\text{SiH} + \text{TiCl}_4$. The study of the reactions of acylferrocenes with SmI_2 is so far

elusive. As acylferrocenes are readily available precursors viable to derivatization for the preparation of catalysts and materials [7], their reactivity towards SmI_2 is worthwhile to investigate.

2. Results and discussion

Table 1 lists the results of the reactions of acylferrocenes **1a–c** and **2** with SmI_2 in THF solution. In the presence of H_2O (11 equiv.), the reaction of ferrocenecarbaldehyde (**1a**) with SmI_2 (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 SmI_2 (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 $\text{SmI}_2/\text{H}_2\text{O}$ (entry 5) resulted in a decreased yield (61%) of **4b**. Deoxygenation of benzoylferrocene (Eq. (1)) and 1,1'-diacetylferrocene (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

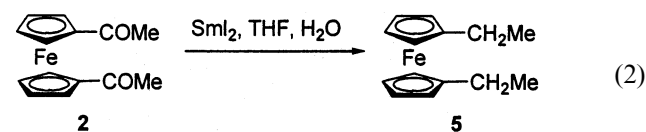
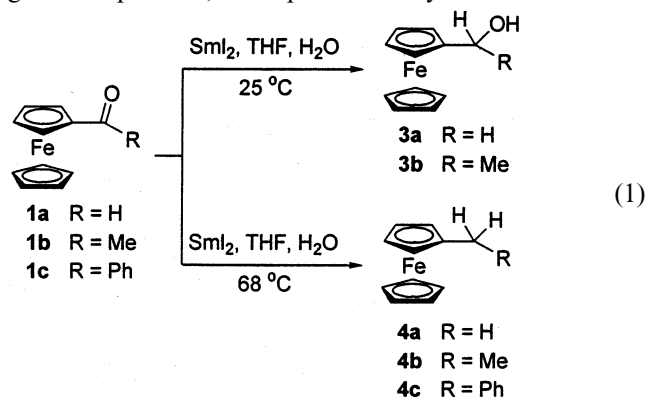
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Table 1
The reactions of acylferrocenes **1a–c** and **2** with SmI_2 in THF solution

Entry	Substrate	SmI_2 /substrate molar ratio	Additive	Reaction temp./°C	Reaction time	Products (yield/%)
1	1a	2.6	H_2O (11 equiv.)	25	10 min	3a (93)
2	1b	2.6	H_2O (11 equiv.)	25	10 min	3b (92)
3	1a	8	H_2O (20 equiv.)	68	4 h	4a (70)
4	1b	8	H_2O (20 equiv.)	68	24 h	4b (85)
5	1b	4	H_2O (8 equiv.)	68	4 h	4b (61)
6	1c	8	H_2O (20 equiv.)	68	16 h	4c (44)
7	2	16	H_2O (40 equiv.)	68	16 h	5 (67)
8	1a	8	None	68	48 h	6 (42) ^a
9	1b	8	None	68	48 h	7 (20)+ 8 (43) ^a
10	1b	8	Sieves (200 mg)	68	48 h	7 (25)+ 8 (36) ^a
11	1b	8	HMPA (0.6 equiv.)	68	48 h	7 (23)+ 8 (36) ^a
12	1b	8	HMPA (1.4 equiv.)	68	48 h	7 (18)+ 8 (51) ^a

^a 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%).

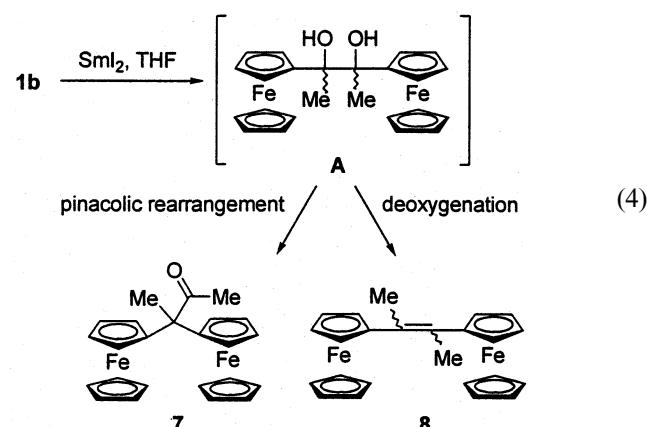
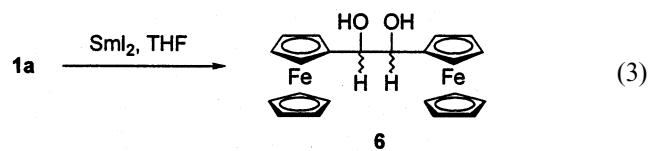
ferrocenyl alcohols with an excess of SmI_2 , and these processes might be facilitated by the in situ generated Sm(III) ion of Lewis acid nature. Indeed, 1-ferrocenylethanol (**3b**) reacted with $\text{SmI}_2/\text{H}_2\text{O}$ in refluxing THF gave ethylferrocene (**4b**), the anticipated deoxygenation product, in a quantitative yield.



In the absence of H_2O , 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 SmI_2 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 ^1NMR 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/TiCl_4 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 SmI_2 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 SmI_2 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 HClO_4 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 [δ_{H} 7.26, δ_{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_2O_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-diiodoethane (500 mg, 1.8 mmol) in anhydrous THF (18 ml) for 1.5 h at room temperature (r.t.). After addition of H_2O (135 mg, 7.5 mmol), the mixture was cooled in an ice bath, and a solution of **1b** (160 mg, 0.7 mmol) in THF (5 ml) was added. After stirring for 10 min at 0°C, the reaction was quenched by ice water (2 ml). The mixture was filtered through a pad of silica gel column, and the filtrate was concentrated to give a practically pure product of **3b** (148 mg, 92%).

3.2.1. Ferrocenylmethanol [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%). $^1\text{H-NMR}$ (CDCl_3 , 200 MHz) δ 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). $^{13}\text{C-NMR}$ (CDCl_3 , 50 MHz) δ 60.6, 67.9 (2 C), 68.2 (7 C), 88.1.

3.2.2. 1-Ferrocenylethanol [4a], **3b**

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz) δ 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). $^{13}\text{C-NMR}$ (CDCl_3 , 50 MHz) δ 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-diiodoethane (2.25 g, 8.0 mmol) in anhydrous THF (70 ml) for 1.5 h at r.t. After addition of H_2O (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**

$^{13}\text{C-NMR}$ (CDCl_3 , 50 MHz) δ 14.8, 67.1 (2 C), 68.5 (5 C), 69.1 (2 C), 83.9. Anal. Calc. for $\text{C}_{11}\text{H}_{12}\text{Fe}$: 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 $^1\text{H-}$ and $^{13}\text{C-NMR}$ analyses. $^{13}\text{C-NMR}$ (CDCl_3 , 50 MHz) δ 14.6, 22.2, 66.8 (2 C), 67.4 (2 C), 68.3 (5 C), 91.0. Anal. Calc. for $\text{C}_{12}\text{H}_{14}\text{Fe}$: 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), benzoylferrocene (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). $^{13}\text{C-NMR}$ (CDCl_3 , 50 MHz) δ 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). $^{13}\text{C-NMR}$ (CDCl_3 , 50 MHz) δ 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 $\text{MeOH-H}_2\text{O}$ to give the pinacols **6** (90 mg, 42%) as a mixture of two stereomers (1:1). $^1\text{H-}$

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 C₂₄H₂₄Fe₂: C, 67.96; H, 5.70. Found: C, 67.67; H, 5.60.

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