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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.

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

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, Zn(Hg) + HCl (Clemmensen reduction), $LiAlH_4 + AlCl_3$, $NaBH_4 + ZnCl_2$, $NaBH_3CN + BF_3$, $NaBH_3CN + TiCl_4$ and $Et_3SiH + TiCl_4$. 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 SmI_2/H_2O (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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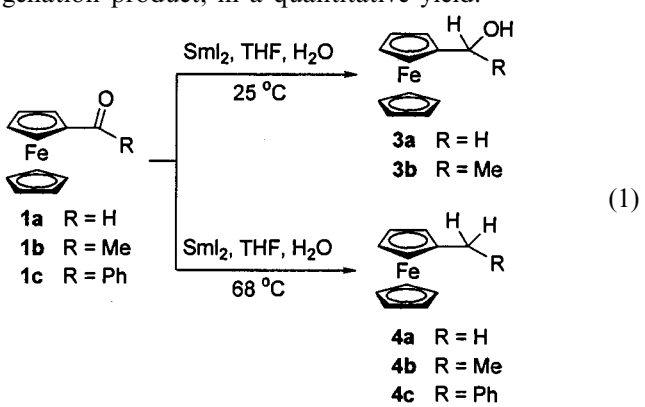
Table 1
The reactions of acylferrocenes **1a–c** and **2** with SmI_2 in THF solution

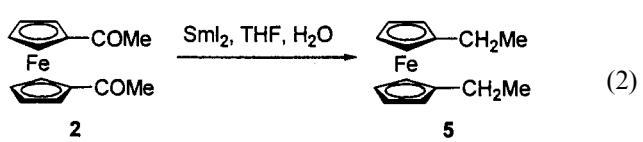
Entry	Substrate	SmI_2/substrate molar ratio	Additive	Reaction temp./°C	Reaction time	Products (yield/%)
1	**1a**	2.6	H_2O (11 equiv.)	25	10 min	**3a** (93)
2	**1b**	2.6	H_2O (11 equiv.)	25	10 min	**3b** (92)
3	**1a**	8	H_2O (20 equiv.)	68	4 h	**4a** (70)
4	**1b**	8	H_2O (20 equiv.)	68	24 h	**4b** (85)
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 SmI_2/H_2O in refluxing THF gave ethylferrocene (**4b**), the anticipated deoxygenation product, in a quantitative yield.



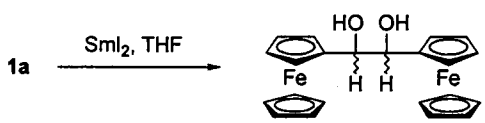
(1)



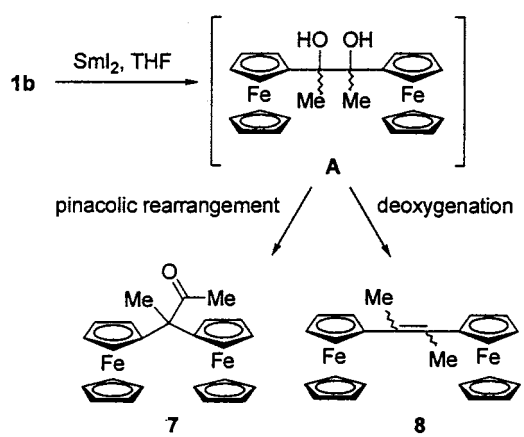
(2)

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 ^{1}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 $Zn/TiCl_4$ 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)



(4)

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}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}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}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}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}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 $C_{11}H_{12}Fe$: 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) δ 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), 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}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}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 × 10). The extracts were combined, washed with water, concentrated, and crystallized from MeOH–H_2O to give the pinacols **6** (90 mg, 42%) as a mixture of two stereomers (1:1). ^{1}H-

NMR ($CDCl_3$, 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 SmI_2 in the absence of water.

Acetylferrocene (228 mg, 1 mmol) was treated with SmI_2 (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***

^{1}H-NMR ($CDCl_3$, 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). ^{13}C-NMR ($CDCl_3$, 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***

^{1}H-NMR ($CDCl_3$, 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); ^{1}H-NMR ($CDCl_3$, 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 $C_{24}H_{24}Fe_2$: C, 67.96; H, 5.70. Found: C, 67.67; H, 5.60.

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