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Unexpected reactions of ferrocene acetal derived from tartaric acid with alkyllithium: competition between proton abstraction and nucleophilic attack

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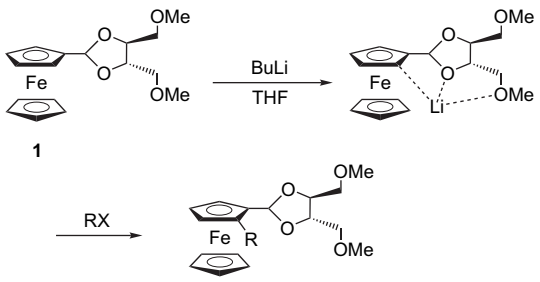
Abstract—We wished to prepare planar chiral compounds by the lithiation of acetal 2-ferrocenyl-(4*S*,5*S*)-bis(methoxymethyl)-1,3-dioxolane (**1**) with butyllithium followed by the reaction with an electrophile. However, the desired products were not observed and two unexpected products, 1-ferrocenyl-1-pentanol (**4**) of the nucleophilic attack product and 2-ferrocenyl-4,5-dimethylene-1,3-dioxolane (**5**) of the proton abstraction product, were isolated. Because the nucleophilic attack on acetal carbon is rarely reported so far and both products **4** and **5** may have some potential uses in organic synthesis, these unexpected reactions are investigated in detail. The mechanisms of these reactions are discussed.

1. Introduction

In recent years, ferrocene ligands with planar chirality have been studied and showed high activities and selectivities in many kinds of asymmetric reactions.[1] Currently there is much effort devoted to their design and synthesis. Ugi method[2] has been widely applied to prepare ferrocenyl compounds with planar chirality, and the strategy using *ortho*-directing groups as the attached chirality auxiliary is a key process for the creation of planar chirality.[3–11] A number of chiral *ortho*-directing substituents, such as sulfoxides,[3] acetals,[4] oxazolines,[5] hydrazones,[6] azepines,[7] sulfoximines,[8] pyrrolidine,[9] *O*-methyl ephedrine derivatives,[10] and oxazaphospholidine-oxide,[11] have been studied. Some of these *ortho*-directing groups, such as oxazoline moiety, can be used as ligands as it is. Some cannot be used directly, and need to be modified further. On the other hand, the ferrocenyl ligands with only planar chirality as chiral element have attracted the interest of many chemists for their excellent asymmetric catalytic activity.[12] To synthesize such ligands, it is necessary to remove central chirality or to destroy the *ortho*-directing chiral groups. Since acetal group as the *ortho*-directing auxiliary can be removed under mild conditions,[4] we set up a new route to introduce a planar chirality element to 2-ferrocenyl-(4*S*,5*S*)-bis(methoxymethyl)-1,3-dioxolane (**1**), which could be readily prepared from ferrocenecarboxaldehyde and available dimethyl L-tartrate, and transformation of which to an achiral aldehyde derivative would occur under mild conditions as known. Then, it should be rationalized that by coordination of the organolithium species to acetal oxygen, diastereoselective *ortho*-lithiation of **1**, followed by the reaction with electrophilic reagents such as chlorodiphenylphosphine, would result in the introduction of planar chirality (Scheme 1). However, different from our expectation, the lithiation of ferrocene acetal **1** with butyllithium did not occur at the Cp ring of the ferrocene, and two competitive reactions, proton abstraction and nucleophilic attack at the acetal group, were observed. Here we want to report this unexpected result of the lithiation of ferrocene acetal **1**.



Scheme 1.

Keywords: Lithiation; *ortho*-Directing groups; Ferrocene; Butyllithium; Dimethyl L-tartrate; Ferrocene acetal; Ferrocene alcohol.
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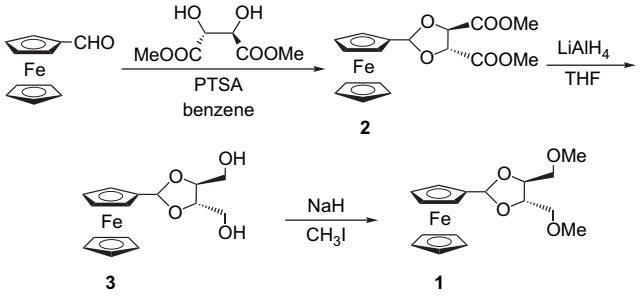
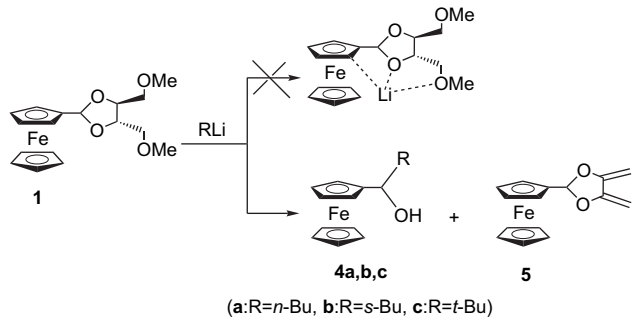
2. Results and discussion

As shown in Scheme 2, ferrocene acetal **1** was readily prepared from ferrocenecarboxaldehyde and commercially available dimethyl L-tartrate in three steps. A benzene solution of ferrocenecarboxaldehyde and 1 equiv dimethyl L-tartrate was heated to reflux in the presence of 0.1 equiv *p*-toluenesulfonic acid monohydrate for 13 h under simultaneous azeotropic removal of the resulting water. After work-up, an acetal intermediate **2** was obtained in 60% isolated yield. Then **2** was reduced by lithium aluminum hydride in THF to acetal diol intermediate **3** in the isolated yield of 51%. Next, diol **3** was treated with sodium hydride in THF and then reacted with iodomethane to afford acetal **1** in 96% isolated yield.



Scheme 2.

Then, attempt to prepare the planar chiral compounds, the lithiation of acetal **1** followed by the reaction with an electrophile, was undertaken. However, the desired products were not observed and two unexpected products, ferrocenyl alcohol **4** of the nucleophilic attack product and ferrocenyl diene **5** of the proton abstraction product, were isolated (Scheme 3). Because the nucleophilic attack on acetal carbon is rarely reported so far,[13] and ferrocene alcohol **4** and diene **5** may have some potential uses in organic synthesis, particularly, **4** has been used in investigations of the stereochemistry of nucleophilic substitution reactions at the chiral center and so on,[14] these unexpected reactions were then examined in detail.



Scheme 3.

First, the effects of the additive, the solvent, and the kind of butyllithium on the yields of the two products were investigated using **1**. The results are summarized in Table 1.

The results indicate that all of the above factors have effect on the two competitive reactions, namely the proton abstraction and nucleophilic attack reactions. When **1** was treated with *n*-butyllithium in ether, the proton abstraction reaction predominated and **5** was isolated as the main product (entry 1). When TMEDA was added to the above reaction system, the reaction became slower and nucleophilic attack product **4** was isolated as the main product (entry 2). The change of solvents from ether to THF and toluene also slows down the reactions and **4** was isolated as the main product (entries 3 and 4). We may also conclude that higher yield of **4** could be achieved with a bulkier alkyllithium (entries 1, 5, and 6). *s*-Butyllithium also afforded **5** as the main product. However, *tert*-butyllithium provided **4** as the main product in 53% yield. The ee of **4c** in entry 6 was determined as 54% by an ^{1}H NMR analysis using Eu(hfc)$_3$ as chiral shift reagent and the optical rotation of **4c** was determined to be +43°, by which the main enantiomer of **4c** was deduced to have an *S*-configuration.[14a]

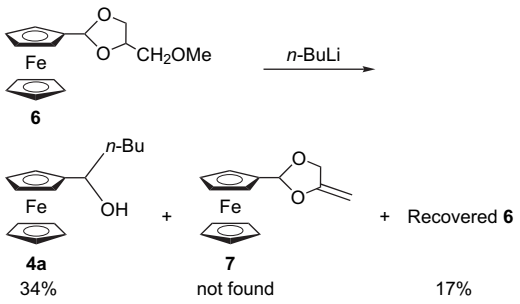
Table 1. Competition of proton abstraction and nucleophilic attack toward acetal **1** with butyllithiums[a]

Entry	BuLi	Solvent	Time (h)	Yield (%)[b]		
				4	**5**	Recovered **1**
1	*n*-BuLi	Ether	5.5	6	52	Trace
2	*n*-BuLi	Ether[c]	12	31	14	31
3	*n*-BuLi	THF	12	16	6	34
4	*n*-BuLi	Toluene	12	22	18	25
5	*s*-BuLi	Ether	1	14	52	Trace
6	*t*-BuLi	Ether	6	53	22	Trace

[a] Reactions were conducted at rt, except entry 6, which was carried out at −78 °C. The ratio of acetal **1**/butyllithium is 1:2.4.
[b] Isolated yield.
[c] TMEDA added (1 equiv to butyllithium).

Next, in order to investigate the reaction mechanism, the isolated diene **5** was treated with *n*-butyllithium in ether at room temperature for 10 h. No reaction was observed. This showed that the alcohol product **4** is not produced via diene **5**.

Then, ferrocene acetal **6** was prepared as a mixture of two diastereomers via the condensation of ferrocenecarboxaldehyde with glycerol followed by a methylation with iodomethane. The reaction of acetal **6** with *n*-butyllithium also afforded nucleophilic attack product **4a**, but no proton abstraction product **7** was observed (Scheme 4). This result, as well as the fact that **5** is inert toward *n*-butyllithium, indicates that for nucleophilic attack on acetal carbon, the chelation of two molecules of butyllithium with the oxygen atoms in acetal ring and methoxy groups is necessary. Therefore, a plausible mechanism for nucleophilic attack reaction of **6** and **1** can be elucidated as in Figures 1 and 2, respectively, although no reasonable by-product for identification was obtained. For the lithiation of **1**, the nucleophilic attack on acetal carbon would be suggested to occur on the side of acetal ring by butyllithium chelated with the methoxy oxygen on the bottom face of acetal ring trans to ferrocene, where it would be less hindered than from the top face of acetal ring (Fig. 2). The (*S*)-product of **4** obtained with *tert*-butyllithium also supported this postulation.



Scheme 4.

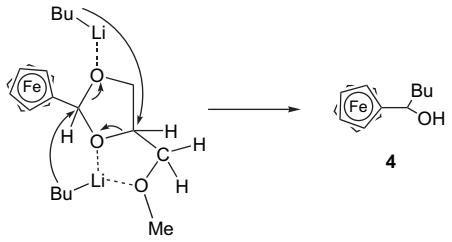


Figure 1.

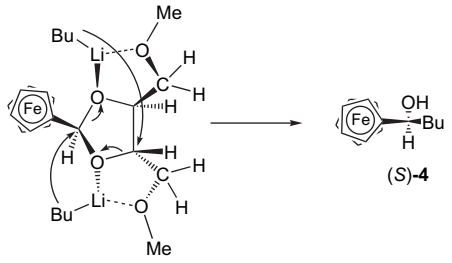


Figure 2.

Since no proton abstraction product **7** was afforded from the reaction of acetal **6** with *n*-butyllithium, a plausible mechanism for the reaction of proton abstraction is presented as shown in Figure 3. The two butyllithium molecules are chelated with two methoxy groups simultaneously, and the two protons are pulled out by each butyl anion nearby. With the butyllithium bearing a bulkier group or *n*-butyllithium combined with TMEDA, it would be more difficult for Li(I) to be chelated with two methoxy groups simultaneously.

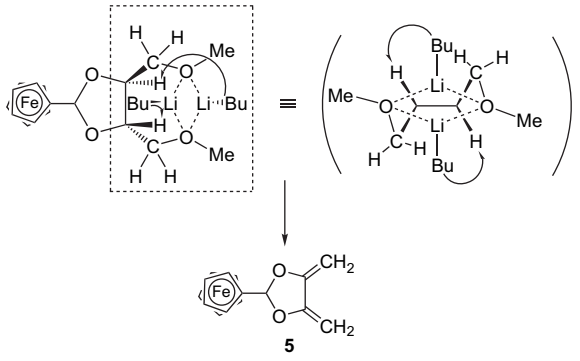


Figure 3.

The experimental results strongly supported this proposed mechanism (entries 1, 5, and 6 in Table 1).

3. Conclusions

In summary, for the preparation of planar chiral compounds, the lithiation of acetal **1** followed by the reaction with electrophile was conducted. However, the desired products were not found and two unexpected products, ferrocenyl alcohol **4** of the nucleophilic attack product and ferrocenyl diene **5** of the proton abstraction product, were isolated. It is clear that the nucleophilic attack and proton abstraction reactions occurred competitively, since the ratio of the two products changes with the change of reaction conditions. Their plausible mechanisms were proposed.

4. Experimental

4.1. General

Optical rotations were measured on a DIP-181 digital polarimeter. ^{1}H NMR spectra were recorded on a JEOL GSX-400 spectrometer and the chemical shifts were referenced to $CHCl_3$ (δ 7.27) in $CDCl_3$. The fast atom bombardment mass spectra (FAB-MS) and high-resolution mass spectra (HRMS) were obtained on a JEOL JMS-DX303HF spectrometer.

THF, ether, and toluene were freshly distilled from sodium and TMEDA from CaH_2 before use. All of the other chemicals used in synthetic procedures were of reagent grade. Merck 70–230 mesh silica gel was used for column chromatography. TLC plastic sheet (Silica gel 60 F_{254}) was used for the determination of R_f. All of the reactions were carried out under an argon atmosphere.

4.1.1. 2-Ferrocenyl-(4*S*,5*S*)-bis(methoxycarbonyl)-1,3-dioxolane 2. A solution of ferrocenecarboxaldehyde (3.9 g, 18.0 mmol), dimethyl L-tartrate (3.2 g, 18.0 mmol), and *p*-toluenesulfonic acid monohydrate (0.034 g, 0.18 mmol) in benzene (20 mL) was heated to reflux for 13 h under simultaneous azeotropic removal of the resulting water. The mixture was diluted with benzene, and neutralized with Na_2CO_3 powder. The neutralized solution was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure. The resulting residue was purified by chromatography (ethyl acetate–hexane 1:5) to provide the desired compound **2** (4.10 g, 60%). R_f=0.07 (ethyl acetate–hexane 1:5). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.10 (s, 1H), 4.92 (d, *J* 3.7 Hz, 1H), 4.79 (d, *J* 4.0 Hz, 1H), 4.50 (br, 1H), 4.39 (br, 1H), 4.24 (s, 5H), 4.21 (br, 2H), 3.88 (s, 3H), 3.82 (s, 3H).

4.1.2. 2-Ferrocenyl-(4*S*,5*S*)-bis(hydroxymethyl)-1,3-dioxolane 3. To a suspension of $LiAlH_4$ (0.82 g, 22 mmol) in dry THF (60 mL) was added **2** (4.1 g, 11 mmol) in dry THF (40 mL) within 35 min at 0 °C. The reaction mixture was heated to reflux for 3 h. To the reaction mixture, water (3.2 mL) and 4 M NaOH (1.2 mL) were added successively and slowly at 0 °C to quench the reaction. The solvent was evaporated and the residue was dissolved in dichloromethane (20 mL), and dried over $MgSO_4$. After

filtration, the filtrate was concentrated under reduced pressure. The resulting residue was purified by chromatography (ethyl acetate) to provide the desired compound **3** as a yellow solid (1.7 g, 51%). R_f=0.30 (ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.94 (s, 1H), 4.37–4.33 (m, 2H), 4.22–4.20 (m, 2H), 4.21 (s, 5H), 4.13–4.10 (m, 2H), 3.89–3.73 (m, 4H), 2.06–1.99 (m, 2H).

4.1.3. 2-Ferrocenyl-(4*S*,5*S*)-bis(methoxymethyl)-1,3-dioxolane 1. To a suspension of sodium hydride (0.40 g, 17 mmol) in dry THF (16 mL) was added **3** (1.7 g, 5.5 mmol) in dry THF (30 mL) at 0 °C and stirred for 0.5 h. To the mixture was added iodomethane (1.30 mL, 21 mmol) at 0 °C, then, the reaction mixture was stirred at room temperature overnight. The reaction mixture was diluted with dichloromethane, then washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure. The resulting residue was purified by chromatography (ethyl acetate–hexane 1:2) to provide the desired compound **1** (1.8 g, 96%). R_f=0.30 (ethyl acetate–hexane 1:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.89 (s, 1H), 4.35 (br m, 2H), 4.20 (s, 5H), 4.16 (br m, 2H), 4.14–4.09 (m, 1H), 4.06–4.01 (m, 1H), 3.63–3.52 (m, 4H), 3.45 (s, 3H), 3.43 (s, 3H). HRMS (FAB) calcd for $C_{17}H_{22}O_4Fe$: 346.0868, found: 346.0869. $[\alpha]_D^{14}$ +7.29 (*c* 1.10, $CHCl_3$).

4.1.4. 2-Ferrocenyl-4-methoxymethyl-1,3-dioxolane 6. A solution of ferrocenecarboxaldehyde (1.5 g, 7.0 mmol), glycerol (0.7 g, 7.6 mmol), *p*-toluenesulfonic acid monohydrate (0.070 g, 0.37 mmol) in benzene (20 mL) was heated to reflux for 6 h under simultaneous azeotropic removal of the resulting water. The mixture was diluted with ether, washed with brine, and then dried over Na_2SO_4. The solvent was removed under reduced pressure. The resulting residue was purified by flash chromatography (ethyl acetate–hexane 1:2) to provide the desired corresponding acetal compound (1.10 g). To a suspension of sodium hydride (0.28 g, 12 mmol) in dry THF (16 mL) was added the above acetal compound (1.10 g) in dry THF (40 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 0.5 h. To the mixture, iodomethane was added, and the reaction mixture was stirred for 20 min at 0 °C and then for 1.5 h at room temperature. Methanol was added to quench the reaction. The reaction mixture was diluted with ether, washed with brine, and then dried over $MgSO_4$. The solvent was removed under reduced pressure. The resulting residue was purified by chromatography (ethyl acetate–hexane 1:2) to provide the desired compound **6** (0.39 g, 18% for two steps). But the two diastereomers of **6** could not be separated. The ^{1}H NMR of **6** showed two sets of signals in a ratio of 1:1 and some of the signals are overlapped. R_f=0.33 (ethyl acetate–hexane 1:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.90 (s, 1H), 5.75 (s, 1H), 4.36–4.34 (m, 2H), 4.34–4.28 (m, 4H), 4.21 (s, 5H), 4.20 (s, 5H), 4.19–4.16 (m, 5H), 4.03 (dd, *J* 8.4, 7.0 Hz, 1H), 3.88 (dd, *J* 8.1, 5.5 Hz, 1H), 3.77 (dd, *J* 8.1, 6.2 Hz, 1H), 3.59–3.43 (m, 4H), 3.44 (s, 3H), 3.41 (s, 3H). HRMS (FAB) calcd for $C_{15}H_{18}O_3Fe$: 302.0605, found: 302.0603.

4.2. General procedure for treatment of compound 1 with butyllithium

In a typical run, to a solution of acetal compound **1** (0.91 g, 2.6 mmol) in dry ether (30 mL) was added slowly 1.56 M *n*-butyllithium (4.1 mL, 6.3 mmol) within 60 min and the mixture was then stirred for 5.5 h at room temperature. The reaction mixture was concentrated under reduced pressure and the residue was dissolved in dichloromethane. The solution was washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure. The resulting residue was subjected to chromatography (ethyl acetate–hexane 1:20) to provide compound **4a** (dark yellow oil, 0.042 g, 6%) and **5** (dark yellow oil, 0.381 g, 52%) (entry 1 in Table 1).

4.2.1. 1-Ferrocenylpentan-1-ol 4a. R_f=0.07 (ethyl acetate–hexane 1:20). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.34–4.29 (m, 1H), 4.26–4.24 (m, 1H), 4.21 (s, 5H), 4.20–4.15 (m, 3H), 1.93 (d, *J* 3.7 Hz, 1H), 1.73–1.53 (m, 2H), 1.49–1.25 (m, 4H), 0.91 (t, *J* 7.3 Hz, 3H). HRMS (FAB) calcd for $C_{15}H_{20}OFe$: 272.0864, found: 272.0864.

4.2.2. 2-Methyl-1-ferrocenylbutan-1-ol 4b. R_f=0.23 (ethyl acetate–hexane 1:10). There are two sets of signals with a rate of 1:1 in the spectrum of ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.27–4.14 (m, 10H), 4.22 (s, 5H), 4.21 (s, 5H), 2.14 (d, *J* 1.5 Hz, 1H), 2.05 (d, *J* 1.8 Hz, 1H), 1.61–1.38 (m, 4H), 1.15–0.81 (m, 11H), 0.73 (d, *J* 7.0 Hz, 3H). HRMS (FAB) calcd for $C_{15}H_{20}OFe$: 272.0864, found: 272.0879.

4.2.3. 2,2-Dimethyl-1-ferrocenylpropan-1-ol 4c. R_f=0.14 (ethyl acetate–hexane 1:20). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.38–4.09 (m, 9H), 3.97 (s, 1H), 0.88 (s, 9H). HRMS (FAB) calcd for $C_{15}H_{20}OFe$: 272.0864, found: 272.0845. $[\alpha]_D^{15}$ +43 (*c* 0.5, $CHCl_3$), 54% ee, mp 78.0–82.0 °C.

4.2.4. 2-Ferrocenyl-4,5-dimethylene-1,3-dioxolane 5. R_f=0.31 (ethyl acetate–hexane 1:20). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.31 (s, 1H), 4.52 (d, *J* 2.9 Hz, 2H), 4.49 (d, *J* 2.9 Hz, 2H), 4.34 (m, 2H), 4.25 (s, 5H), 4.23 (m, 2H). HRMS (FAB) calcd for $C_{15}H_{14}O_2Fe$: 282.0343, found: 282.0343.

Acknowledgements

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