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Hydroiminoacylation of Allyl Alcohol with Ferrocenecarboxaldimine by Rh(I) catalyst

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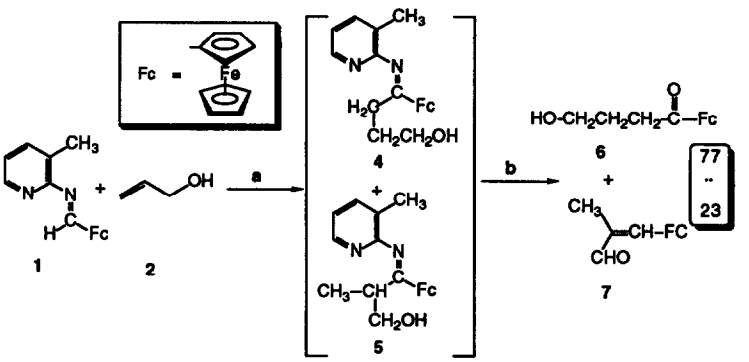
Abstract: The hydroiminoacylaction of allyl alcohol with ferrocenecarboxaldimine by Wilkinson's complex produces 4-hydroxy-1-butanoyl ferrocene and 3-ferrocenyl-2-methyl-2-propanal after hydrolysis of the resulting ketimines.

Acylferrocenes are particularly important in the synthesis of alkyl ferrocenes and of alkenyl ferrocenes[1]. The major pathway for preparing acylferrocene is Friedel-Crafts acylation[2], in which one of limitations is the choice of alkyl group of acylchloride due to non-availability of hydroxyalkyl acylchloride. Already new synthetic method of acylferrocene through hydroiminoacylation of the terminal olefins with ferrocene-carboxaldimine has been reported[3]. Even poly-butadiene can be used for hydroiminoacylation substrate to prepare polymer-supported acylferrocene[4]. This paper reports hydroiminoacylation of allyl alcohol with ferrocenecarboxaldimine and elucidation of the isomerization and dehydration mechanism for hydroxyalkyl acylferrocene during the hydrolysis process.

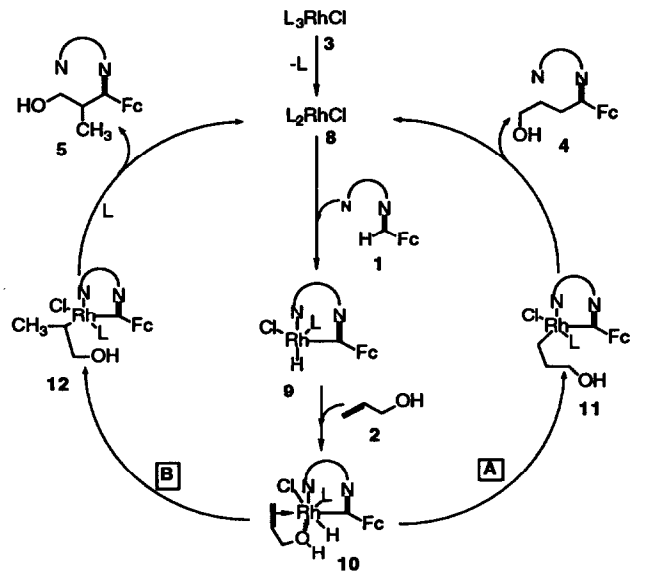


(Scheme 1) a: $(PPh_3)_3RhCl$ (3) (10 mol %), toluene, 110°C, 24h. b: (i) 1N HCl aq. sol. (ii) extracted by $CHCl_3$ (iii) separated by column-chromatography

Allyl alcohol is a good candidate for hydroiminoacylation substrate because hydroacylation of allyl alcohol with ferrocenecarboxaldimine (1) may produce an acylferrocene having a hydroxy group. Compound 1 (0.33 mmol) reacted with allyl alcohol (2) (0.66 mmol) at 110°C for 24h in 2 ml toluene under Wilkinson's complex (3) (0.033 mmol: 10 mol% based upon 1) as catalyst (Scheme 1). Without isolation of the resulting hydroiminoacylation products, they were hydrolyzed with 1 N HCl aq. solution for 2h to give 4-hydroxy-1-butanoylferrocene (6) and 3-ferrocenyl-2-methyl-2-propanal (7) in a 77:23 ratio in 72 % yield after

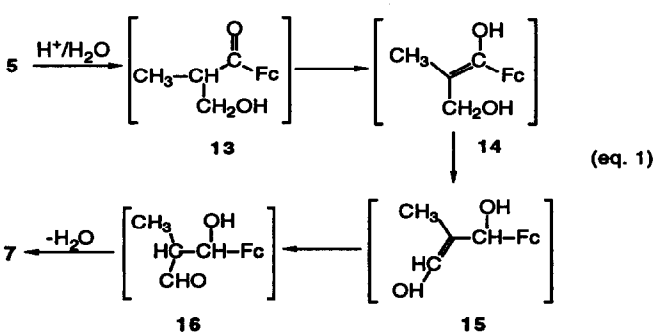
chromatographic isolation[5].

The mechanism can be easily inferred from the above results. The first step must be the formation of the rhodium(III) hydride **9** *via* C-H bond cleavage of aldimine **1** by Rh(I) of **8**[6](scheme 2).



(Scheme 2) Mechanism for the hydroiminoacylation of 2 with 1

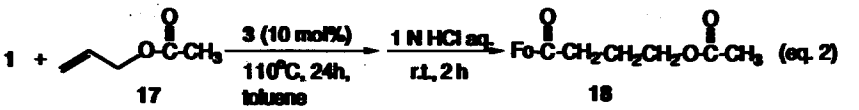
The hydride insertion into allyl alcohol gives two hydrometallated complexes as intermediates, **11** and **12**, according to anti-Markownikoff's rule and Markownikoff's rule respectively. Reductive-elimination of **11** and **12** produce two ketimines, **4** and **5**. Since these ketimines were hardly isolated as pure forms due to the partial hydrolysis during the column-chromatographic isolation, they were hydrolyzed completely by 1N HCl aq. solution to give the final products, **6** and **7**. While compound **6** is the expected anti-Markownikoff's linear alkyl acyferrocene product, **7** is the unexpected hydrolysis product of **5**.



(eq. 1)

Hydrolysis of the ketimine 5 must generate the secondary alkyl acylferrocene 13 as an intermediate (eq. 1). The enolization of acylferrocene 13 might produce vinylalcohol 14, which can be easily isomerized to the aldehyde 16 through 15. There seems no Rh(I) catalyst's involvement in the transformation of 14 to 15 because Wilkinson's complex might be decomposed or deactivated in this acidic aqueous solution. Dehydration of 16 suppose to give 7 as a final product since α-hydroxyalkyl ferrocene is very susceptible for dehydration producing alkenyl ferrocenes[7]. It has been reported that ferrocenylbutadiene can be prepared by pyrolysis of 4-ferrocenyl-1-buten-4-ol over alumina since the thermodynamically stable conjugate diene connected with the ferrocenyl group is generated by dehydration of the α-hydroxyalkenyl ferrocene[8]. Formation of the stable conjugate α,β-unsaturated aldehyde connected with the cyclopentadienyl group in 16 must be the driving force for dehydration process even under the mild conditions. From the above results, the ratio of two hydrometallations of anti-Markownikoff's and Markownikoff's can be measured as a 77 : 23. Usually hydroacylation of a 1-alkene like 1-pentene produces only a linear-alkyl acylferrocene, according to anti-Markownikoff's rule[6]. The reason for the partial formation of 5, Markownikoff's product, must be that allyl alcohol in 10 might coordinate the oxygen atom as well as olefin, which make an easier hydride transfer to the terminal olefinic carbon to generate a transient stable metallacycle complex in allyl alcohol than in 1-alkene having a capability of only one olefin coordination.

When allyl acetate (17), in which the hydroxy group of allyl alcohol is protected by the acetyl group, was applied for this hydroiminoacylation under the identical reaction conditions, only a linear hydroacylated product, 4-acetoxy-1-butanoylferrocene (18)[9], was obtained exclusively in 81 % yield (eq.2)[10].



Any acyloxy derivative of 13, 14, or 15 has not been isolated, informing that the reaction takes place according to anti-Markownikoff's rule, differently from the results of the hydroiminoacylation of allyl alcohol. The reason must be that allyl acetate may not act as a bidentate ligand in the olefin coordination. Vigorous acid hydrolysis of the acetate ester 18 in co-solvent system (1 N HCl aq. sol : acetone = 5 : 2) at 100°C for 1h results in 6 in 76 % yield after chromatographic isolation.

The results indicate that allyl alcohol can be hydroiminoacylated with ferrocenecarboxaldimine to give both linear and branched acylferrocene without being interrupted by the hydroxy group, and the branch hydroxyalkyl acylferrocene undergoes isomerization under the acid hydrolysis condition. The selectivity for the anti-Markownikoff's product can be improved by protecting the hydroxy group of allyl alcohol with the acetyl group.

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5. 6: ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 4.80 (t, J=1.95 Hz, 2H, 3,4-Hs in substituted Cp ring), 4.51 (t, J=1.94 Hz, 2H, 2,5-Hs

in substituted Cp ring), 4.21 (s, 5H, unsubstituted Cp ring), 3.75 (t, J=6.8 Hz, 2H, CH_2-O), 2.89 (t, J=6.85 Hz, 2H, CH_2-CO), 1.98 (q, J=6.5 Hz, β-CH_2 to CO); ^{13}C NMR (50.5 MHz, $CDCl_3$) δ (ppm) 78.5 (C-1 in substituted Cp ring), 72.4 (C-3,4 in substituted Cp ring), 69.5 (Cs in unsubstituted Cp ring), 69.4 (C-2,5 in substituted Cp ring), 62.6 (CH_2-OH), 36.6 (CH_2-CO), 26.9 (β-CH_2 to CO); IR (neat) 3600-3200 (OH), 3100, 2920, 1660 (Fe-CO), 1450, 1410, 1380, 1250, 1108, 1050, 1000, 825, 535, 485 cm^{-1}; mass spectrum; m/e (assignment) 254 (M^+-H_2O), 186 (FeH^+), 185 (Fe^+); Anal Calcd for $C_{12}H_{14}O_2Fe$: C, 65.6; H, 6.25. Found: C, 63.5; H, 5.91.; TLC R_f = 0.29, hexane : ethylacetate = 1 : 1, SiO_2. 7: ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 9.46 (s, 1H, -CHO), 7.1 (s, 1H, -CH=), 4.80 (t, J=1.6 Hz, 2H, 3,4-Hs in substituted Cp ring), 4.49 (t, J=1.7 Hz, 2H, 2,5-Hs in substituted Cp ring), 4.16 (s, 5H, substituted Cp ring), 1.93 (d, J=0.83 Hz, 3H, CH_3-); ^{13}C NMR (50.5 MHz, $CDCl_3$) δ (ppm) 194.5 (CHO), 151.5 (=C-CHO), 134.6 (Fe-CH=), 71.4 (C-2,5 in substituted Cp ring), 71.0 (C-3,4 in substituted Cp ring), 69.2 (Unsubstituted Cp ring), 10.5 (CH_3-); IR (neat) 3090, 2900, 1670 (COH, vs), 1615 (vs), 1450, 1330, 1250, 1160, 1105, 1050, 1000, 925, 820, 500 cm^{-1}; mass spectrum; m/e (assignment) 254 (M^+), 226 (M^+-CO), 225 (M^+-CHO); Anal Calcd for $C_{13}H_{14}OFe$: C, 66.14; H, 5.51. Found: C, 64.42; H, 6.13.; TLC R_f = 0.79, hexane : ethylacetate = 5 : 2, SiO_2.

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9. 17: ^{1}H NMR (200 MHz, $CDCl_3$) δ (ppm) 4.78 (t, J=1.9 Hz, 2H, 2,5-Hs in substituted Cp ring), 4.5 (t, J=1.9 Hz, 2H, 3,4-Hs in substituted Cp ring), 4.19 (s, 5H, unsubstituted Cp ring), 4.17 (t, J=6.4 Hz, 2H, CH_2O), 2.80 (t, J=7.2 Hz, CH_2CO), 2.06 (s, $COCH_3$), 2.05 (m, 2H, β-CH_2 to CO); ^{13}C NMR (50.5 MHz, $CDCl_3$) δ (ppm) 203.0 (Fe-CO), 170.9 (CH_3CO), 78.8 (C-1 in substituted Cp ring), 72.2 (C-2 & 5 in substituted Cp ring), 69.7 (Unsubstituted Cp ring), 69.2 (C-3 & 4 in substituted Cp ring), 63.8 (OCH_2-), 35.6 (α-CH_2 to CO), 23.2 (β-CH_2 to CO), 20.9 (CH_3CO); IR (neat) 3100, 2960, 1732 (CH_3CO), 1665 (Fe-CO), 1450, 1380, 1365, 1240 (vs), 1110, 1040, 825, 540, 485 cm^{-1}; mass spectrum; m/e (assignment) 314 (M^+), 254 (M^+-Cp), 227 (Fe(OH)-CH_2), 212 (M^+-Cp-CH_3CO), 185(Fe^+); Anal Calcd for $C_{15}H_{18}O_3Fe$: C, 61.2; H, 5.73. Found: C,62.5; H,6.07.; TLC R_f = 0.61, hexane : ethylacetate = 5 : 2, SiO_2.
10. Additional 7 % of the ester-hydrolysis product, 6, was obtained.

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