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Alkyl Lewis Acid Catalyzed Syntheses of Dicarbonyl Ferrocenes

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A series of diferrocenoyl compounds; succinyl (**1**), glutaryl (**2**), adipoyl (**3**), suberoyl (**4**) and sebacoyl ferrocene (**5**) were synthesized from the reaction of ferrocene with $EtAlCl_2$. Compared to the conventional methods reported in the literature, the yields obtained from these reactions are found to be higher than the typical catalyst.

Key Words: Diferrocenoyl ketones, Ferrocenoyls, Ferrocene derivatives, Alkyl Lewis acid, Bronsted base, Acylation.

INTRODUCTION

Diferrocenoyl ketones are valuable intermediates. They have been found in a number of applications and utilized in many areas such as in self-assembled monolayers[1], in Langmuir-Blodgett films[2], in chiral building blocks for asymmetric reactions[3] and in detecting group electronegativies[4]. Although there have been a good deal of reports in the literature associated with the synthesis of ferrocenyl ketones, only a few methods is available for the synthesis of dicarbonyl diferrocenyl ketones. Typical Freidel-Craft acylation employing $AlCl_3$ as a Lewis acid catalyst[3,5-7] is one of the most convenient method described. The oxidative dimerization of acetyl ferrocene[8,9] and β-oxidation of acylferrocenes[10] are the other methods reported. Previous studies conducted on the synthesis of ferrocenyl ketones clearly indicate that better yields are accessible especially those for unsaturated ferrocenylenones when alkyl Lewis acids were used in acylation in return for typical Lewis acid[11]. Alkyl Lewis acids can act both Lewis acids and Bronsted bases, although they are weaker in comparison with $AlCl_3$ or $FeCl_3$. This novel property of alkyl Lewis acids was first monitored by Snider *et al.*[12] and applying this particular synthetic methodology using alkyl Lewis acids as catalyst have been proven to be highly successful in the ene reactions[13-15]. As part of our ongoing study of the synthesis of dicarbonyl ferrocene complexes[11,16], it is decided to use alkyl Lewis acid ($EtAlCl_2$) as catalyst due to the difficulties of forming acylation reactions of ferrocene in the case of ferrocene as starting materials[11,17].

EXPERIMENTAL

All reactions were performed under a dry atmosphere of nitrogen. Dibasic acid chlorides (Aldrich), ferrocene (Merck) and $EtAlCl_2$ (Aldrich, 1 M in hexane) were used as received. Dichloromethane was distilled over CaH_2 prior to use. ^1H and ^{13}C NMR spectra were recorded on Bruker-Spectroscopin Avance DPX400 Ultra-Shield spectrometer with TMS as standard. The solid state Fourier transform infrared spectra (KBr pallets, 4000-400 cm^{-1}) were recorded on Perkin Elmer FTIR 1600 and selective peaks are reported.

General procedure for the syntheses of saturated diferrocenoyl compounds: Under nitrogen, a solution of ferrocene (1.184 g, 0.00636 mol) in dry CH_2Cl_2 (10 mL) was treated with $EtAlCl_2$ (6.9 mL, 1 M in hexane, 0.0069 mol) at 0 ºC and after 1 h stirring, the colour of the solution changed from bricket red to dark blue and gas evolution was clearly observed. To this solution, glutaryl chloride (369 μL, 0.00289 mol) was added dropwise for 3 min. The resulting mixture was allowed to stir for 1 h. During the work-up, the crude product was hydrolyzed with NH_4Cl (25 mL), extracted with $CHCl_3$ (3 times, in total 60 mL), dried over $MgSO_4$ and concentrated *in vacuo*. Upon purification with flash column (eluted with 4:1, EtOAc:hexane), 289 mg unchanged recovery ferrocene and glutaryl ferrocene (**2**) (903 mg) were obtained (67 %). ^1H NMR (δ, ppm): 2.057 (2H, s), 2.77 (4H, broad s), 4.133 (10H, unchanged two Cp ferrocene rings, broad s), 4.43 (4H, Fc, broad s), 4.75 (4H, Fc, broad s). ^{13}C NMR (δ, ppm): 19.48, 38.84, 69.37, 69.82, 72.28, 79.027, 204.21. IR (KBr, ν_{max}, cm^{-1}): 1664, 1458, 1241, 835.

Succinylferrocene (1): General procedure was applied for the synthesis of compound **1**. The crude product was purified with flash column (eluted with $CHCl_3$ under atmospheric pressure). Yield: (47 %) ^1H NMR (δ, ppm): 3.05 (4H, broad s), 4.20 (10H, unchanged two Cp ferrocene rings, broad s), 4.40 (4H, Fc, broad s), 4.76 (4H, Fc, broad s). ^{13}C NMR (δ, ppm): 32.93, 69.25, 69.92, 71.89, 78.91, 202.10. ^{13}C NMR (δ, ppm): 32.93, 69.25, 69.92, 71.88, 78.92, 202.1. IR (KBr, ν_{max}, cm^{-1}): 1663, 1455, 1241, 1065, 821.

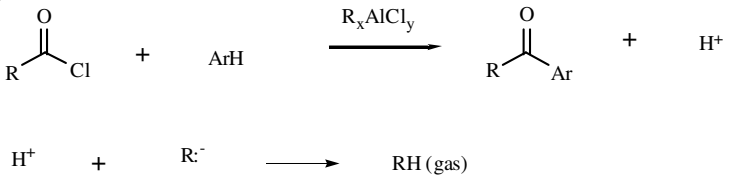
Adipoylferrocene (3): General procedure was applied for the synthesis of compound **3**. The crude product was purified with column chromotagraphy (eluted with $CHCl_3$ under atmospheric pressure). Yield: (88 %) ^1H NMR (δ, ppm): 1.79 (4H, m), 2.74 (4H, m), 4.17 (10H, unchanged two Cp ferrocene rings, broad s), 4.45 (4H, Fc, broad s), 4.76 (4H, Fc, broad s). ^{13}C NMR (δ, ppm): 24.31, 39.48, 69.27, 69.68, 71.92, 79.17, 203.29. IR (KBr, ν_{max}, cm^{-1}): 1657, 1450, 1371, 1258, 1070, 829.

Suberoylferrocene (4): General procedure was applied for the synthesis of compound **4**. The crude product was purified with column chromotagraphy (eluted with 3:1, EtOAc:hexane). Yield: (40 %) ^1H NMR (δ, ppm): 1.38 (4H, broad s), 1.67 (4H, broad s), 2.62 (4H, t, 7 Hz), 4.10 (10H, unchanged two Cp ferrocene rings, s), 4.35 (4H, Fc s), 4.69 (4H, Fc s). ^{13}C NMR (δ, ppm): 24.30, 29.36, 39.49, 69.27, 69.66, 71.88, 79.24, 203.58.

Sebacoylferrocene (5): General procedure was applied for the synthesis of compound **5**. The crude product was purified with column chromotagraphy (eluted with 5:1, EtOAc:hexane). Yield: (90 %) ^{1}H NMR (δ, ppm): 1.40 (8H, broad s), 1.72 (4H, broad s), 2.70 (4H, t 6 Hz), 4.19 (10H, unchanged two Cp ferrocene rings, broad s), 4.47 (4H, Fc broad s), 4.77 (4H, Fc broad s). ^{13}C NMR (δ, ppm): 24.55, 29.42, 29.52, 39.69, 69.32, 69.70, 72.00, 79.22, 204.18.

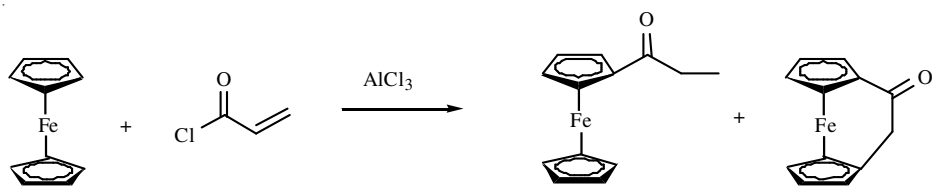
RESULTS AND DISCUSSION

Alkyl Lewis acids display considerably different characteristics than non-alkyl Lewis acids (*i.e.*, $AlCl_3$, $FeCl_3$ *etc*.) towards cations in the acylation reactions owing to the fact that they readily eliminate the hydrogens produced during the acylation (**Scheme-I**).



Scheme-I: Proton elimination produced during aromatic acylation

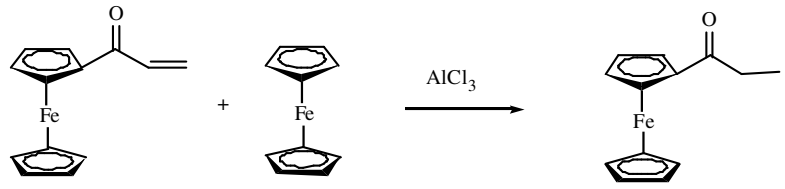
Previous reports clearly illustrate that acylation of ferrocene with acryloyl chloride would not yield the corresponding unsaturated ferrocenyl ketone, instead afforded saturated ketone (*i.e.*, propanoyl ferrocene) and ferrocenophane derivative when $AlCl_3$ was used as a catalyst[17] (**Scheme-II**).



Scheme-II: Acylation of ferrocene using $AlCl_3$

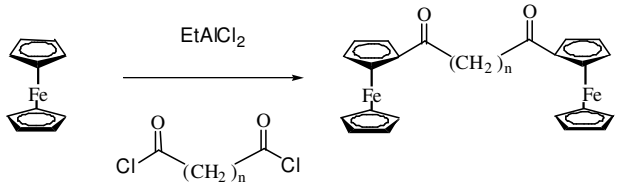
Acryloyl ferrocene can simply be converted into propanoyl ferrocene in the presence of both $AlCl_3$ and ferrocene (**Scheme-III**). The excellent reductivity of ferrocene and $AlCl_3$ was also viewed by various groups and even some of those obtained acryloyl ferrocene in good yield employing alkyl Lewis acids as catalysts[11,18].

Keeping in mind, the fact that the synthesis of acryloyl ferrocene from $AlCl_3$ and ferrocene is easily accessible, we were interested in studying in detail more general pathways to acryloyl ferrocene by applying alkyl Lewis acid as catalyst. In the present work, the syntheses of succinyl (**1**)[18], glutaryl (**2**), adipoyl (**3**), suberoyl (**4**)



Scheme-III: Reduction of acryloyl ferrocenes

and sebacoyl ferrocenes (**5**) were achieved by the reaction of ferrocene and corresponding acid chlorides using $EtAlCl_2$ catalyst (**Scheme-IV**). The yields for (**1**), (**2**), (**3**), (**4**) and (**5**) were found to be as 47, 67, 88, 40 and 90 %, respectively. To the best of our knowledge, the yields obtained from using this synthetic methodology are the best yields reported in the literature. Although higher yields for the synthesis of succinyl ferrocene (**1**) were published, those method involve two steps and follow the reaction mechanism reported as oxidative coupling of acetyl ferrocenes[8,9]. We have also reported the molecular structure of compound (**1**) previously[16]. In the crystal structure, two ferrocenyl groups are found to be almost *trans* to each other (Fig. 1).



1 n: 2 Succinyl ferrocene, 47%
2 n: 3 Glutaryl ferrocene, 67%
3 n: 4 Adipoyl ferrocene, 88%
4 n: 6 Suberoyl ferrocene, 40%
5 n: 8 Sebacoyl ferrocene, 90%

Scheme-IV: Syntheses of diferrocenoyl compounds

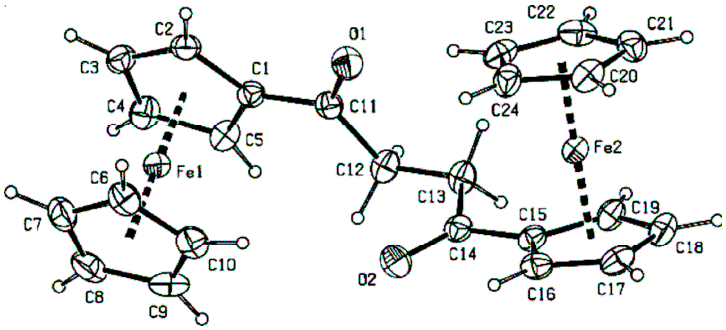


Fig. 1. Ortep diagram of compound **1**

It is interesting to note that the synthesis of adipoyl ferrocene (**3**) yielded only the target product (**3**) as a sole product without any side product formation. It is already reported in literature that this product obtained with the yield 28 % by using $AlCl_3$[6]. However, the resulting major product involving mainly through the

aldol condensation reaction was found to be 1-ferrocenylcarbonyl-2-ferrocenylcyclopentene with the yield 56 %. Up to the present, the highest yield for the synthesis of (**3**) has been reported to be as 78 % by using $AlCl_3$ however the synthetic methodology followed was quite different in protocol[7]. Using $AlCl_3$ catalyst low yields varying between 20.0 and 35.7 % were obtained for the synthesis of (**2**)[3,5]. Compound (**4**) and (**5**) have also been prepared as side products during the synthesis of unsymmetrical ketones[19]. Despite the fact that the synthesis of (**5**) from ferrocene has been reported to take place in three steps[20], the synthesis was smoothly accomplished with 90 % yield in one step.

Conclusion

$EtAlCl_2$, alkyl Lewis acid, have been proven to be efficient catalysis for the diacylation of ferrocene. Yields obtained from syntheses are moderate but higher than the previous works. As a result, alkyl Lewis acids can possibly be applied as catalysts for the synthesis of diferrocenoyl ketones as well as ferrocenylenones[11].

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