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Further solvent-free reactions of ferrocenylaldehydes: Synthesis of 1,1′-ferrocenyldiimines and ferrocenylacrylonitriles

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Dedicated to the memory of my Mother, Kathleen Mary Imrie.

Abstract

Grinding of 1,1′-ferrocenedicarboxaldehyde with a 2.2 molar equivalent of an aromatic amine in a solvent-free environment provided excellent yields of 1,1′-ferrocenyldiimines. After mixing the aldehyde and amines, a gum or melt formed which eventually solidified to the product. An analytically pure sample of the product was obtained by cold recrystallization. Grinding of ferrocenecarboxaldehyde and 4-substituted phenylacetonitriles under solvent-free conditions provided good yields of the corresponding ferrocenylacrylonitriles. The yield in this reaction was very low when the substituent group *para* to the acetonitrile group was electron-donating.

Keywords: 1,1′-Ferrocenedicarboxaldehyde; Ferrocenylacrylonitrile compounds; 1,1′-Ferrocenyldiimines; Green chemistry; Solvent-free synthesis

1. Introduction

The solvent-free approach to the synthesis of molecules is an attractive one since the majority of solvents are either toxic or flammable and add considerably to the cost of an overall synthesis. In many instances, the solvent-free approach allows shorter reaction times, improved selectivities and easier separations and purifications than conventional solvents [1]. A monologue has recently appeared on the subject of solvent-free reactions and it provides an up-to-date account of the range of synthetic reactions that have been investigated under solvent-free conditions [2]. One of the current themes in our research is to study the solvent-free synthesis of organometallic molecules, especially ferrocenes and ruthenocenes since this field is relatively undeveloped. The ultimate aim is to use knowledge on simple organometallic molecules to gain an understanding on the molecular parameters required for reactivity in the room temperature grinding of reactants.

Ferrocenecarboxaldehyde (**1**) and acetylferrocene are two important precursors of ferrocene derivatives, and have been shown to be particularly amenable to reaction under solvent-free conditions [3]. For example, it was shown by Imrie et al. that **1** reacts with substituted anilines to provide excellent yields of ferrocenylmonoimines after just a few minutes of grinding [3a]. The reactions took place in most cases at room temperature and the products were isolated by cold recrystallization from a minimal quantity of methanol. This current paper describes our latest results on further reactions of **1** under solvent-free conditions. Furthermore, it reports the first results on the reactivity of 1,1′-ferrocenedicarboxaldehyde under solvent-free conditions.

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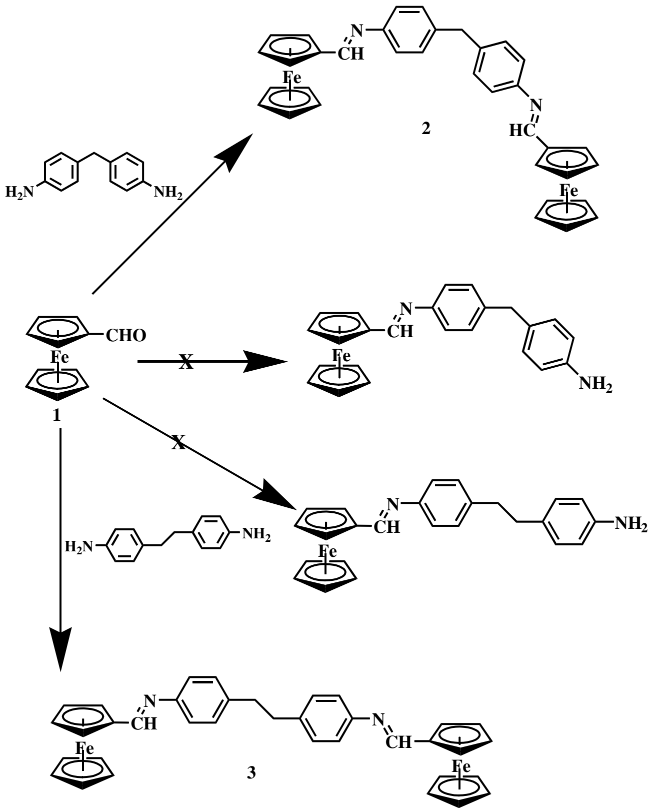
2. Results and discussion

2.1. Solvent-free synthesis of ferrocenylimines

Ferrocenylimines have been conventionally prepared by heating a solution of the ferrocenylaldehyde and aromatic amine in solvents such as methanol or ethanol [4]. This approach usually involves heating the reactants for a few hours under reflux; thermally sensitive ferrocenylimines can suffer a degree of decomposition during this time. During our initial study [3a], it became apparent that **1** was extremely reactive under solvent-free conditions. To investigate this further, we decided to look at its reactivity with anilines and amines containing two amino functional groups. The reactions with anilines are summarized in Scheme 1 and the results again demonstrate the reactivity of **1**. The molar ratio of the reactants, **1**:anilines was varied from 1:2, 1:1 and 2:1. In all cases, bisferrocenylimines **2** and **3** were isolated and the excess unreacted starting materials were recovered. The ratio 2:1 (aldehyde:aniline) had the best atom economy and provided excellent yields of the bisimines.

Compound **4** has been previously reported by Lee et al. [5] and was synthesized by the reaction of **1** with ethylenediamine in diethyl ether in the presence of either a drying agent, magnesium sulfate or catalyst, $RuCl_2(PPh_3)_2$. We have found that simple grinding of **1** with ethylenediamine provides **4** (Fig. 1) in quantitative yield in a few minutes. In contrast to the reactions described in Scheme 1, we found that it was necessary to use an excess of the diamine to achieve a high conversion.



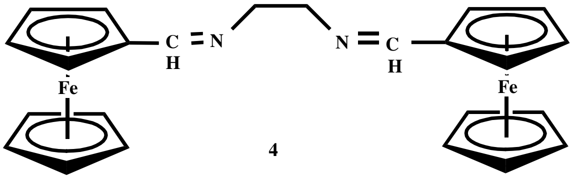
Scheme 1. Solvent-free reactions of **1** with bis(amino) compounds that provide isolated products.

Despite the fact that the first synthesis of 1,1′-ferrocenedicarboxaldehyde (**5**) (Scheme 2) was reported many years ago, the synthesis of simple 1,1′-ferrocenyldiimines (Scheme 2) and other derivatives has not been researched in-depth. This could be due in part to the fact that **5** is not commercially available and the difficulties experienced in its synthesis.

The starting materials used in the synthesis of 1,1′-ferrocenyldiimines were all commercially available apart from **5**. The synthesis of **5** according to the available literature methods [6] proved to be very inefficient, giving consistently isolated yields of less than 10% and involved a tedious work-up procedure. However, with the help of modifications communicated separately to us by Loubser and Kamounah [7], it was possible to modify the literature method to give consistently higher yields. Synthesis of 1,1′-ferrocenyldiimines **6**–**12** was achieved by simply mixing and grinding **5** with the aniline under solvent-free conditions in a 1:2.2 mole ratio (Scheme 2).

The reactions occurred readily. In some cases a gum formed and in others the mixture turned into a melt. Upon solidification, ^{13}C NMR was used to analyze the crude product and to gauge the extent of the reaction. This was easily followed by the disappearance of the carbonyl (C=O) resonance peak of **5** and the appearance of a strong resonance for the imine (C=N) functional group in the range 155.00–165.00 ppm. Minimal amounts of anhydrous methanol were used to recrystallize the products. The results are given in Table 1.

In general, under the equivalent solvent-free conditions, **5** was less reactive than **1**, justifying the slight excess of anilines that were used in these reactions. In a few cases, in order to improve the yield, the pyrex reaction tube was immersed in a constant temperature water bath at 50 °C. The reaction did not work very well in cases where the aniline contained an electron-withdrawing group such as nitro; this could be explained by the electrons being inductively pulled from the amino group causing the aniline to be less reactive in this type of reaction. The ^{1}H NMR spectrum for the 1,1′-ferrocenyldiimines showed a characteristic peak in the region of 8.40–8.20 ppm for the imine protons (CH=N). Its integration represented the two protons that are chemically equivalent.



4

Fig. 1. Structure of *N*,*N*′-ethylenebis[(ferrocenylmethylidene)amine].