Reformatsky Type Addition of α-Bromopropionate to Ketones Promoted by $Fe(CO)_5$

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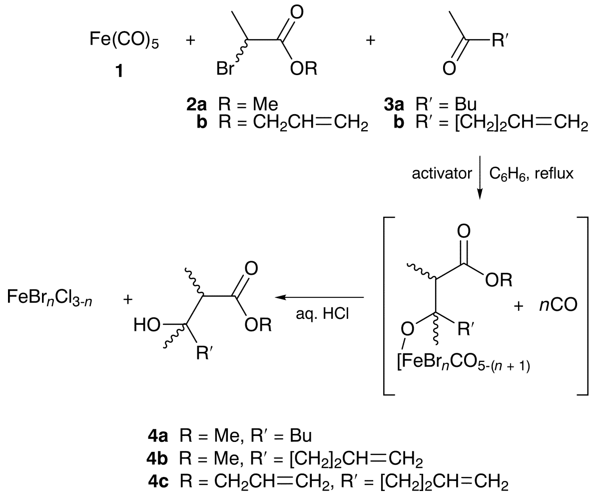
Summary to follow



Scheme 1

We report here the first case of an $Fe(CO)_5$ (**1**) promoted Reformatsky reaction of α-bromopropionates [methyl α-bromopropionate (**2a**) and allyl α-bromopropionate (**2b**)] with methyl butyl ketone (**3a**) or allylacetone (**3b**) in refluxing benzene, giving the addition products **4a**–**c** in chemical yields varying from 60 to 20% (Scheme 1). The addition of small amounts of activators (such as $BrCCl_3$, Br_2 or I_2) was found to be necessary for the reaction to proceed. No products of addition to the C=C bond were detected in the reaction mixture of **1**, **2a** and **3b** or **1**, **2b** and **3b**. The diastereoisomeric ratios of **4a**–**c** formed in the reaction mixtures, were invariably close to 1:1. No products of a higher molecular weight than **4** were detected in the reaction mixture. No products of ketone self-condensation were detected. In fact, the only observed side reaction was the reduction of the initial **2a** and **2b** to the corresponding propanoic esters.

The initial **1**, if present in a 1:1 ratio to the substrate, was decomposed in the course of the reaction. A tentatively assigned structure of the Fe-containing complexes, finally formed in the reaction solution, is shown in Scheme 1 and might reflect an intermediate which decomposed further in the course of the reaction mixture decomposition.

Presently, the mechanism of the Reformatsky-type reaction is not clear. Most likely the initial stage of the reaction constitutes a generation of the radicals from the initial bromopropionates **2a** and **2b** promoted by a low valent Fe-complex *via* one electron reduction. Further reduction of the radical is followed by the transfer of another electron from a low valent Fe-containing complex with the formation of an organometallic compound (by analogy with the SmI_2 mediated Barbier-type reactions[3]) which most likely contains an Fe–enolate complex. The reaction of the organometallic compound with the ketone carbonyl group, followed by the protonation of the intermediate oxygen anion terminated the reaction. The function of the activators could be the oxidation of the initial **1** generating Fe^{II} containing species which catalysed the electron transfer between $Fe(CO)_5$ and **2**. However, the experimental data available, at present, were not sufficient to support any detailed discussion of the mechanism of the reaction.

In conclusion we suggest a new and seemingly promising variation of the Reformatsky reaction with no need for the preliminary activation of the metal and with a cheap and conveniently handled initial material. Further study of the reaction, including new substrates and the addition of different activators is in progress.

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