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Preliminary communication

Addition of alkyllithium and Grignard reagents to tetracarbonyliron complexes of α,β-unsaturated esters

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Abstract

Addition of alkyllithium and Grignard reagents to the tetracarbonyliron complexes of methyl acrylate (1) and methyl crotonate (2) leads to the production of 4-ketoesters via acyl transfer from the metal to the β carbon of the α,β-unsaturated ester.

Conversion of prochiral α,β-unsaturated esters to their tetracarbonyliron derivatives generates chiral complexes which have considerable potential for undergoing stereoselective reactions to produce specifically substituted esters. In this context, the outcome of nucleophilic attack on tetracarbonyliron complexes of α,β-unsaturated esters is of interest. It has previously been reported that treatment of the tetracarbonyliron complex of methyl β-benzoylacrylate with methoxide or thiophenoxide ion leads to metal–ligand cleavage and reduction of the carbon–carbon double bond [1]. Addition of stabilised carbanions to the tetracarbonyliron complexes of methyl acrylate (1) and methyl crotonate (2) results in direct addition of the nucleophile to the β carbon of the α,β-unsaturated ester and the isolation of Michael-type products in high yield [2]. We report here the consequence of adding alkyllithium and Grignard reagents to the tetracarbonyliron complexes of methyl acrylate (1) and methyl crotonate (2).

Complex **1** was prepared from $Fe_2(CO)_9$ and methyl acrylate by a published procedure [3]. Methyllithium was added to a solution of **1** in diethyl ether at −22°C, and after 1 h the mixture was quenched with a proton source (t-butyl bromide). Filtration of the resulting mixture through alumina to remove iron residues followed by preparative TLC led to the isolation of methyl 4-ketopentanoate (Table 1, Entry 1).

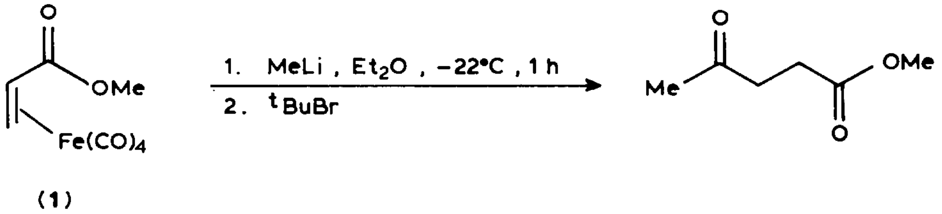

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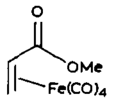
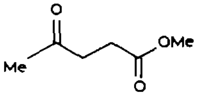
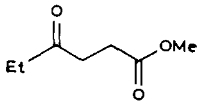
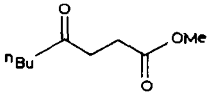
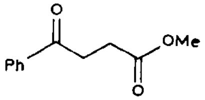
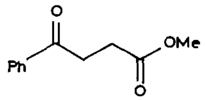
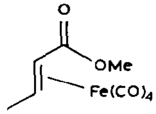
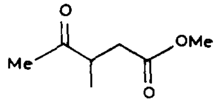
Table 1

Addition of alkyllithium and Grignard reagents to (methyl acrylate) Fe(CO)$_4$ (1) and (methyl crotonate)Fe(CO)$_4$ (2)

Entry	Complex^a	RLi or RMgBr^b	Temperature (°C)	Time (h)	Product^c	Yield (%)
1	 (1)	MeLi	−22	1		41
2		EtMgBr	−22	1		24
3		n-BuLi	−78	6		36
4		PhLi	−22	1		59
5		PhLi	−78	6		67
6	 (2)	MeLi	−78	6		31

^{a} Reactions performed on 0.75–1.00 mmol scale. ^{b} 1.5 equivalents. ^{c} Products were identified by full characterisation or by comparison of their spectroscopic data with literature values.

Similarly, treatment of **1** with ethylmagnesium bromide, n-butyllithium, or phenyllithium gave a 4-ketoester (Table 1, Entries 2–4). Changing the reaction temperature from −22 to −78°C appears to have very little effect on the course of the reaction (Table 1, Entries 4 and 5).

The tetracarbonyliron complex of methyl crotonate (**2**) was prepared from $Fe_2(CO)_9$ and the α,β-unsaturated ester [2b,3]; treatment of **2** with methyllithium also gave a 4-ketoester (Table 1, Entry 6).

Thus, in contrast to the direct addition of stabilised carbanions to the α,β-unsaturated ester ligand of **1** and **2** [2], alkyllithium and Grignard reagents add to a carbonylmetal ligand to form an acylmetal anion which is subsequently transferred to the β-carbon of the α,β-unsaturated ester. This difference in reactivity between stabilised carbanions and alkyllithium/Grignard reagents is also observed in the chemistry of (1,3-cyclohexadiene)Fe(CO)$_3$ [4].

Our results represent the intermediate case between the reactivity of tricarbonyliron complexes of α,β-unsaturated ketones towards alkyllithium reagents, where an acyl group is transferred to the η^4-ligand [5], and the unreactivity of coordinatively saturated acyl ferrates ($RCOFe(CO)_4^-$) towards Michael acceptors, where the acyl group fails to transfer to the uncoordinated Michael acceptor [6].

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