Nucleophilic Addition to Iron Tricarbonyl Complexes of α,β-Unsaturated Ketones

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Reaction of Grignard and organolithium reagents with iron tricarbonyl complexes of α,β-unsaturated ketones leads to 1,4-diketones in a reaction controlled by the transition metal centre.

Although iron tricarbonyl complexes of α,β-unsaturated ketones were first synthesised more than twenty years ago,[1] the reactivity of the α,β-unsaturated ketone fragment of these compounds has received little attention. Electrophilic addition to the complexes has been reported[2,3] but the reaction of iron tricarbonyl complexes of α,β-unsaturated ketones with nucleophiles has not been investigated. This communication describes the reaction of iron tricarbonyl complexes of α,β-unsaturated ketones with Grignard and organolithium reagents resulting in the formation of 1,4-diketones.

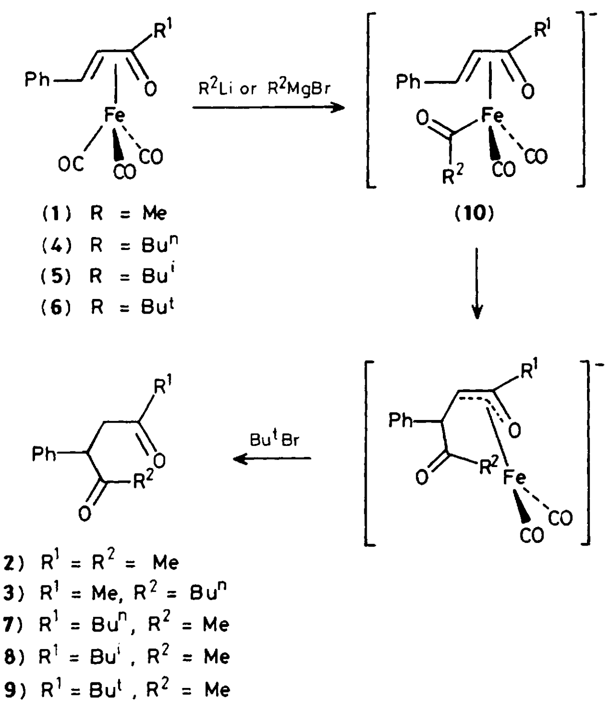
Tricarbonyl(benzylideneacetone)iron (**1**) is readily prepared from benzylideneacetone and enneacarbonyldi-iron.[2] Complex (**1**) was treated with methylmagnesium bromide at −78 °C and then quenched with t-butyl bromide as a proton source. Removal of iron residues by filtration through alumina and column chromatography led to the isolation of the 1,4-diketone (**2**) (Table 1, entry 1). Similarly, treatment of (**1**) with methyl-lithium and butyl-lithium resulted in the formation of 1,4-diketones (**2**) and (**3**) respectively (Table 1, entries 2 and 3).

The reaction is unaffected by varying the carbonyl substituent R^1. The novel complexes (**4**), (**5**), and (**6**) were prepared from enneacarbonyldi-iron and the corresponding α,β-unsaturated ketones. Treatment of enneacarbonyldi-iron with α,β-unsaturated ketones carrying substituents at the α-carbon atom did not lead to the isolation of stable complexes.

Table 1. Addition of Grignard and organolithium reagents to iron tricarbonyl complexes of α,β-unsaturated ketones.[a]

Entry	Complex	R^2Li or R^2MgBr	Product[b] (% yield)[c]
1	(**1**)	MeMgBr	(**2**) (79)
2	(**1**)	MeLi	(**2**) (75)
3	(**1**)	Bu^nLi	(**3**) (53)
4	(**4**)	MeLi	(**7**) (73)
5	(**5**)	MeLi	(**8**) (59)
6	(**6**)	MeLi	(**9**) (64)

[a] Reactions typically involved stirring the iron tricarbonyl complex (0.5 mmol) and the organolithium or Grignard reagent (0.75 mmol) at −78 °C for 7 h in Et_2O. The reaction mixture was quenched with Bu^tBr (5.0 mmol) and allowed to warm to room temperature over 1 h. [b] Products were identified by i.r., n.m.r., and high resolution mass spectra. [c] Yields refer to purified product isolated by column chromatography (SiO_2).



Reaction of (**4**), (**5**), and (**6**) with methyl-lithium resulted in their conversion into the 1,4-diketones (**7**), (**8**), and (**9**) respectively (Table 1, entries 4, 5, and 6).

It has been reported that the metal acyl anions, $[RCONi(CO)_3]^-$ and $[RCOFe(CO)_3]^-$, react in an intermolecular fashion with α,β-unsaturated ketones.[4,5] The reaction described here probably proceeds through a metal acyl intermediate (**10**). Acyl transfer to the α,β-unsaturated ketone and protonation presumably occur whilst the α,β-unsaturated ketone is attached to the metal atom. The use of iron tricarbonyl complexes for acyl addition to α,β-unsaturated ketones should have wide applicability.

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