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The reaction of potassium tetracarbonylhydridoferrate with ethyl acrylate in ethanol

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Abstract

The reaction of $KHFe(CO)_4$ with an excess of ethyl acrylate in ethanol for 30 h at 70 °C leads to ethyl propionate (270% with respect to iron) and diethyl 4-oxopimelate (40% yield with respect to iron), whether in an atmosphere of CO or argon. These reactions are shown to proceed by regioselective addition of $KHFe(CO)_4$ to ethyl acrylate to give an intermediate alkyl tetracarbonylferrate **2** ($M = K$), which has been isolated as the PPN^+ salt. In situ protonation of **2** (or of the isomeric alkyltetracarbonylferrate **10**) by the solvent, and reductive elimination of ethyl propionate generate a coordinatively unsaturated $Fe(CO)_4$ species which, when quenched in situ, gives the corresponding $Fe(CO)_4$(acrylate) complex **9**. In the presence of K_2CO_3 and an excess of ethyl acrylate, **9** affords ethyl propionate in 120% yield with respect to iron, which is consistent with the observed pseudo-catalytic reduction of ethyl acrylate by $KHFe(CO)_4$. The formation of diethyl oxopimelate is thought to involve the isomerisation of **2**, followed by reaction of the resulting alkyltetracarbonylferrate **10** with ethyl acrylate.

Introduction

The reactions of tetracarbonylhydridoferrates M^+, $HFe(CO)_4^-$ with α,β-unsaturated carbonyl compounds have been studied by several authors [1–6]. In aprotic solvents, such as THF, $NaHFe(CO)_4$ regioselectively and irreversibly adds to ethyl acrylate **1** to yield the corresponding alkylferrate **2**, which can be isolated as the PPN^+ salt [3,4]. Reaction of **2** ($M = Na$) with a proton source leads to ethyl propionate, while reaction with alkyl iodides affords functionalized derivatives of ethyl propionate [3,4] (Scheme 1).

In protic solvents, such as methanol, reaction of $NaHFe(CO)_4$ with **1** gives the reduction product of **1** in high yield [2]. Although the mechanism of this reaction has not been studied, some information on it can be obtained from the related

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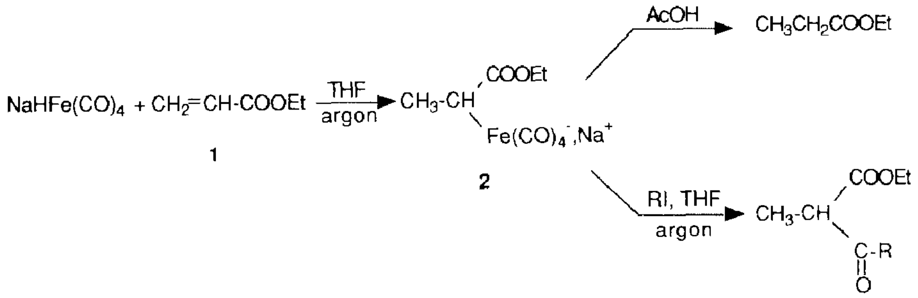
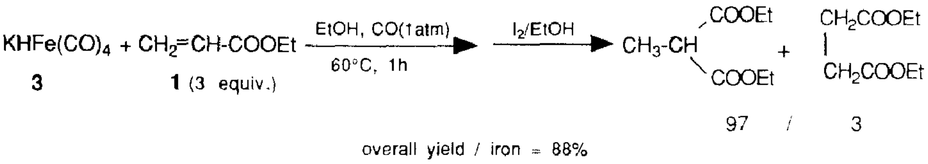


Scheme 1



Scheme 2

functionalization of **1** by a two-step sequence, i.e. reaction with $KHFe(CO)_4$ (**3**) in ethanol, followed by quenching with iodine (Scheme 2) [1].

As part of our interest in developing the use of **3** in organic synthesis and catalysis [7,8], we have reinvestigated the reaction of **3** with ethyl acrylate in ethanol. We report here full details about these reactions and give some mechanistic proposals.

Results and discussion

The conventional way to prepare ethanolic $KHFe(CO)_4$ solutions is to allow $Fe(CO)_5$ (1 equiv.) to react with KOH (3 equiv.) in ethanol at room temperature, according to eq. 1 [9,10].

$$Fe(CO)_5 + 3\ KOH \xrightarrow{EtOH} KHFe(CO)_4 + K_2CO_3 + H_2O \tag{1}$$

When ethyl acrylate is added to this reaction mixture at 70 ° C, the main reaction leads to the formation of ethyl 3-ethoxypropionate (**4**) by the Michael addition of potassium ethoxide to ethyl acrylate (eq. 2,3).

$$EtOH + K_2CO_3 \rightleftharpoons EtOK + KHCO_3 \tag{2}$$

$$\underset{(\mathbf{1})}{CH_2{=}CHCOOEt} \xrightarrow[EtOH]{EtOK} \underset{(\mathbf{4})}{EtOCH_2CH_2COOEt} \tag{3}$$

Preliminary experiments showed that this side-reaction can be suppressed either by filtering off the K_2CO_3 before adding the ethyl acrylate, or, more conveniently, by preparing $KHFe(CO)_4$ from only 2 equiv. of potassium hydroxide (eq. 4).

$$Fe(CO)_5 + 2\ KOH \xrightarrow{EtOH} KHFe(CO)_4 + KHCO_3 \tag{4}$$

The IR spectra of the light pink solutions prepared according to eq. 4 were superimposable (2200–1600 cm^{-1} region) on those obtained according to eq. 1, and showed no traces of unreacted iron pentacarbonyl.

Stoichiometric reactions

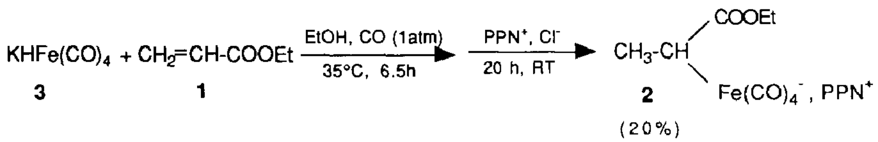
When **1** (11 mmol) is treated with a solution of **3** (prepared from 11 mmol $Fe(CO)_5$ in 50 ml ethanol) for 6 h at 70 °C under an argon atmosphere, a nearly quantitative reduction to ethyl propionate **5** occurred, without the formation of side-products. This is in agreement with the results described by Noyori et al. [2], although the reductions reported by these authors were conducted with a fourfold excess of iron pentacarbonyl.

Careful monitoring by IR analysis throughout the reaction showed the progressive disappearance of the absorption bands of **3** together with the appearance of new bands near 1900 cm^{-1}; these then slowly disappeared to leave bands at 2000 and 1980 cm^{-1}, attributable to $HFe_3(CO)_{11}^-$, as confirmed by the red color of the reaction mixture.

In the reaction of $NaHFe(CO)_4$ with **1** in THF (Scheme 1), it is suggested that the first step of the reaction in ethanol is the addition of **3** to **1**, giving the alkyltetracarbonylferrate **2** (M = K). Protonation by the solvent (or by water introduced with the potassium hydroxide, see Experimental) followed by reductive elimination would lead to ethyl propionate **5**. These hypotheses are supported by the observation that quenching the reaction with an I_2/EtOH solution in the early stages of the reaction leads to the production of diethyl methylmalonate **6** in more than 65% yield (together with traces (< 2%) of diethyl succinate), whereas the same treatment after 4 h leads to **5**, accompanied by only traces of **6**. Carrying out the reaction under carbon monoxide (1 atm) leads, quantitatively, to the same results. This raises a problem with the mechanism of the addition of $KHFe(CO)_4$ to **1** with ethanol as solvent, for it had previously been shown [3,4] that, in THF, the addition of $NaHFe(CO)_4$ to **1** is strongly inhibited by a carbon monoxide atmosphere, which suggests the presence of a dissociative process (eq. 5).

$$HFe(CO)_4^- \xrightleftharpoons{THF} HFe(CO)_3^- + CO \qquad (5)$$

We therefore tried to isolate the postulated alkyltetracarbonylferrate **2** (M = K) as its PPN^+ salt from reaction of **3** with **1** in ethanol under carbon monoxide (1 atm). This was achieved (Scheme 3), although in low yield (20%) because of the loss of product during the separation of **2** from unreacted PPNCl. Spectroscopic data for **2** (IR, ^1H and ^{13}C NMR) are given in Table 1. It therefore appears that the addition of **3** to **1** is not inhibited by a carbon monoxide atmosphere when the solvent is ethanol. The above facts suggest that, whereas the addition of $HFe(CO)_4^-$ to **1** in



Scheme 3

Table 1

Spectroscopic data for **2** ($M = PPN^+$)

IR (CH_2Cl_2)ν(CO): 2000 (m), 1890 (s), and 1660 cm^{-1} (ester)

^1H NMR (CD_2Cl_2, 250 MHz) $[C^1H_3C^2H(Fe(C^6O)_4)C^3O_2C^4H^aH^bC_5H_3]^-$ PPN^+

Chemical shift (δ, ppm)	Assignment
1.18 (t, $^3J(H^5-H^{4a})$ $^3J(H^5-H^{4b})$ 7 Hz)	H on C^5
1.40 (d, ^3J 6.8 Hz)	H on C^1
2.45 (q, ^3J 6.8 Hz)	H on C^2
3.9–4.0 (m (ABX_3), J ($H^{4a}-^{4b}$) 12 Hz)	H^a, H^b on C^4
7.5–7.7	PPN^+

^{13}C NMR (CD_2Cl_2, 62.8 MHz)
$[C^1H_3C^2H(Fe(C^6O)_4C^3O_2C^4H_aH_bC^5H_3]^-$ PPN^+

Chemical shift (δ, ppm)	Assignment
221.3 (s)	C^6
185.2 (s)	C^3
133.2–126.3 (m)	PPN^+
57.9 (t, ^1J(CH) 145 Hz, ^2J(CH) 4 Hz)	C^4
23.7 (q, ^1J(CH) 126 Hz)	C^1
14.5 (d, ^1J(CH) 140 Hz, ^2J(CH) 5,5 Hz)	C^2
14.4 (q, ^1J(CH) 127 Hz, ^2J(CH) 3 Hz)	C^5

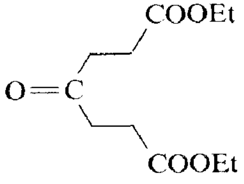
THF follows a dissociative process, a different process occurs in ethanol. Both concerted [3] and radical [11] processes have been shown to occur in the addition of carbonylhydridoferrates on conjugated carbon–carbon double bonds.

Reaction of $KHFe(CO)_4$ with an excess of ethyl acrylate

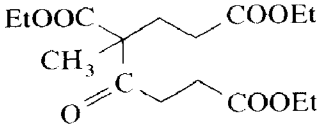
The reaction of **1** (65 mmol) with a solution of **3** (prepared as above, from 10 mmol $Fe(CO)_5$ in 50 ml ethanol) under carbon monoxide (1 atm) was monitored by GC analysis (Table 2). After 30 h at 70 °C, the reaction gave reproducibly a mixture which contained, after quenching with AcOH:

(i) unreacted ethyl acrylate, **1** (17 mmol);
(ii) ethyl 3-ethoxy propionate, **4** (3 mmol);
(iii) ethyl propionate, **5** (27 mmol);
(iv) some traces of diethyl hex-2-enedioate and diethyl methylene 2-glutarate;
(v) two products, **7** and **8**, with larger retention times.

The last two compounds were easily isolated by liquid chromatography. **7** was identified as diethyl-4-oxopimelate by comparison with an authentic sample (see Experimental). The structure given below for **8** is based on spectroscopic data (IR, ^1H, ^{13}C NMR and GC-MS) (see Experimental). They were isolated in yields, relative to $Fe(CO)_5$, of 40 and 5%, respectively.



(**7**)



(**8**)

Table 2

Reaction of ethyl acrylate [a] with $KHFe(CO)_4$ [b] at 70 °C under carbon monoxide (1 atm), followed by quenching with an AcOH/EtOH solution

Time (h)	**1** [c]	**4** [c]	**5** [c]	**6** [c]	**7** [c,d]
0.25	54	–	9	3	–
0.5	43	–	9	2	1
1	41	–	13	2	1
2	32	–	16	1	2
4	26	1	20	–	3
6	24	1	23	–	3
20	18	1	26	–	3
30	17	3	27	–	4

[a] 65 mmol. [b] $Fe(CO)_5$: 10 mmol; KOH: 21 mmol; EtOH: 60 ml. [c] mmol, determined by GC analysis with decane as the internal standard. [d] Compound **8** was also present in low yield.

Further experiments provided the following interesting facts:

(i) use of argon instead of a carbon monoxide atmosphere leads quantitatively to the same results, with the same overall kinetics;

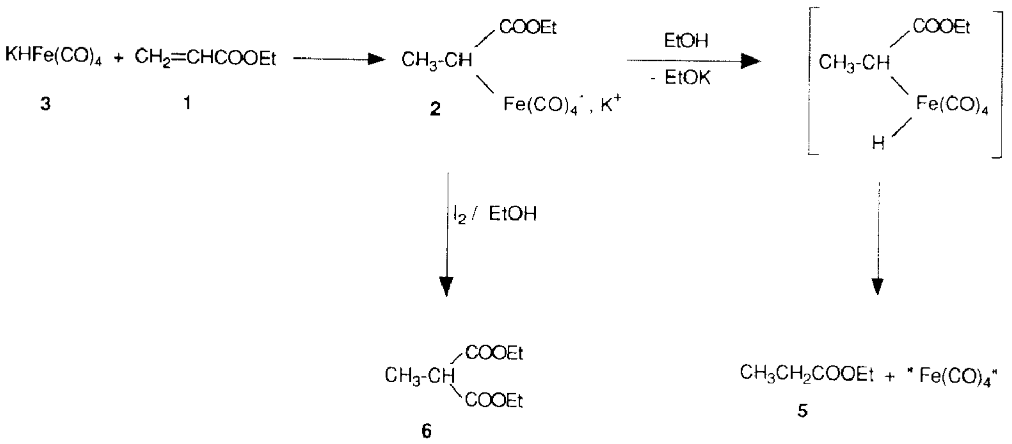
(ii) the IR analysis of the reaction mixture at the end of each reaction indicated the presence of ca. 50% regenerated $Fe(CO)_5$, even for reactions conducted under an argon atmosphere;

(iii) when the reaction was conducted under 20 bar carbon monoxide for 30 h at 70 °C, the yield of reduction products was lowered to 178%/Fe (with 37.5 mmol recovery of **1**) and only small amounts of **7** (and **8**) were formed. No traces of ethyl 2-formylpropionate were detected. IR analysis of the reaction mixture at the end of the reaction indicated the presence of more than 90% regenerated $Fe(CO)_5$.

Thus, it appeared for the first time that the yield in the reduction of **1** to ethyl propionate exceeds the stoichiometric amount with respect to iron (270%), even under argon. This result was quite unexpected as previously reported reductions of α,β-unsaturated carbonyl compounds with $HFe(CO)_4^-$ under similar conditions have been conducted with a fourfold excess of iron pentacarbonyl [2]. Similarly, the reduction of α,β-unsaturated carbonyl compounds by $NaHFe_2(CO)_8$, which is also believed to proceed via **2** (M = Na), has been reported using more than 1 equiv. of the ferrate [3].

Another example is known where $HFe(CO)_4^-$ brings about the reduction of more than 1 equiv. of a carbon–carbon double bond, namely the reduction of enamines under a carbon monoxide atmosphere [12]. However, the stoichiometric yield is not exceed if these reactions are conducted under nitrogen. It was one of the most striking observations of the present study that a carbon monoxide atmosphere is not necessary for the stoichiometric yield with respect to iron to be exceeded in the reduction of ethyl acrylate.

Monitoring of the reaction, by quenching small aliquots with a I_2/EtOH solution, showed that the amount of **2** decreased with time (Table 3). As for the stoichiometric reaction (vide supra), these results suggest that **2** is protonated by the solvent to yield an unstable hydridoalkyltetracarbonyliron complex (The situation is, however, a little more complicated because of the isomerisation of **2**, as we shall



Scheme 4

Table 3

Variation of the amount of **2** with time as indicated by the amount of **6** obtained by quenching aliquots with a I_2/EtOH solution [a,b]

Time (h)	0.25	0.5	1	2	6	20
2 (mmol)	8	7	3	2	0.8	–

[a] Ethyl acrylate: 65 mmol; $Fe(CO)_5$; 10 mmol; KOH: 21 mmol; EtOH: 60 ml; reaction performed at 70 ° C under carbon monoxide (1 atm). [b] Quenching with 2 equiv. I_2/Fe.

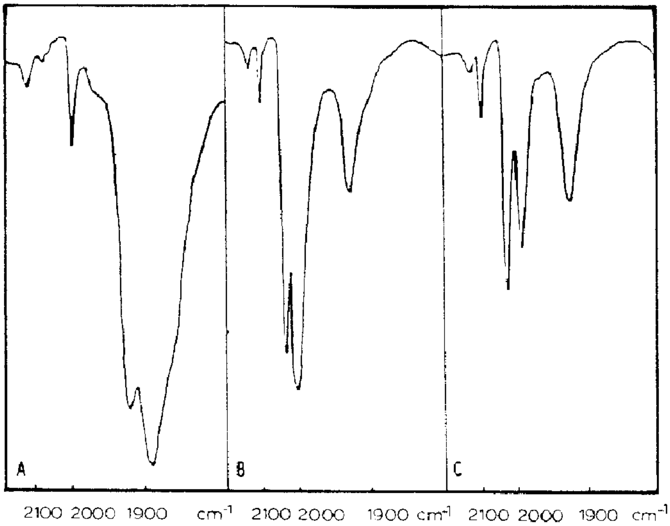
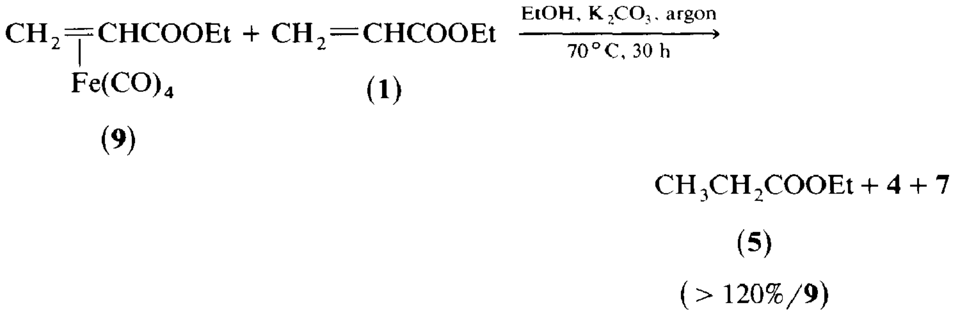


Fig. 1. IR spectra: (in B and C the absorption band at 1930 cm^{-1} is due to EtOH). (A) Ethanolic solution of $KHFe(CO)_4$ before the addition of **1**. (B) Reaction mixture after 6 h at 70 ° C under argon. (C) Complex **9** in EtOH.

see later, eq. 7). Reductive elimination then occurs to give **5** and an unstable iron tetracarbonyl species (Scheme 4).

On the basis of Scheme 4, we suspected that the "$Fe(CO)_4$" moiety could be trapped in situ by excess of **1** to yield the corresponding $Fe(CO)_4$(ethyl acrylate) complex, **9**. This complex was prepared by a known procedure [13] and examination of its IR spectrum showed that it is not easy to show the presence of this complex in a mixture that also contains $Fe(CO)_5$. However, two features may be used to indicate its presence. Firstly, the two strong bands between 2000 and 2040 cm^{-1} that are present in the spectra of both **9** and $Fe(CO)_5$ exhibit inverse relative intensities and, secondly, the $Fe(CO)_4$(ethyl acrylate) complex has a weak band at 2100 cm^{-1}. Examination of the IR spectra of the reaction mixture during the reduction of ethyl acrylate suggested the possible transient presence of **9** (band at 2100 cm^{-1}) (Fig. 1).

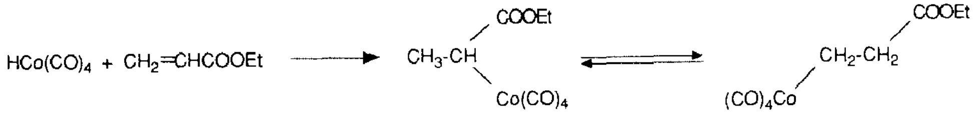
We then examined the stability of **9** in ethanol under our reaction conditions. When **9** was heated in ethanol for 30 h at 70 ° C in the presence of an excess of **1** and $KHCO_3$ (a reagent formed during the preparation of **3** (eq. 4), **5** was formed in a nearly quantitative yield with respect to **9**. This result was quite unexpected since reactions of $Fe(CO)_4$(acrylate) complexes with nucleophiles are known to occur by attack on the carbon–carbon double bond of the acrylate moiety to give the Michael addition product [14]. Nevertheless, this result, which was mentioned briefly by Russian workers twenty years ago [15], may account for yields of reduction product of up to 200%/iron during the reaction of **3** with an excess of **1** in ethanol (vide supra). The reaction was also carried out in the presence of an excess of **1** and K_2CO_3 in order to generate larger amounts of potassium ethoxide, a reagent thought to be formed during the protonation of **2** (Scheme 4). As expected, the main reaction was that giving ethyl 3-ethoxypropionate but ethyl propionate was also formed in more than 120% yield with respect to iron, together with some **7** (eq. 6).



$$\underset{\substack{Fe(CO)_4 \\ (\mathbf{9})}}{CH_2{=}CHCOOEt} + \underset{(\mathbf{1})}{CH_2{=}CHCOOEt} \xrightarrow[70\,°C,\ 30\ h]{EtOH,\ K_2CO_3,\ argon} \underset{\substack{(\mathbf{5}) \\ (>120\%/\mathbf{9})}}{CH_3CH_2COOEt} + \mathbf{4} + \mathbf{7} \qquad (6)$$

Although the mechanisms of the above reactions are not clear at the present time, these results may explain the fact that the yield in the reduction of **1** by **3** reaches values higher than 200%. Lastly, when the reduction of **1** with **3** is conducted under carbon monoxide (vide supra), the "$Fe(CO)_4$" species may be trapped, at least in part, by carbon monoxide, to give $Fe(CO)_5$ at the expense of **9**. The yield of **5** according to eq. 6 is thus lowered (to 178%) and the amount of recovered $Fe(CO)_5$ increased.

The formation of **7** and **8**, which result from in situ carbonylation is also noteworthy for the alkyl ferrate **2** does not readily insert carbon monoxide as do simple alkyl ferrates $RFe(CO)_4^-$. The reason for this lies in the electron-withdraw-

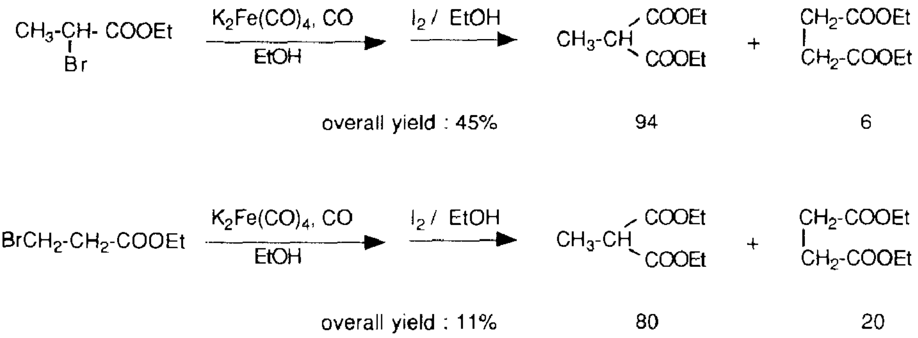


Scheme 5

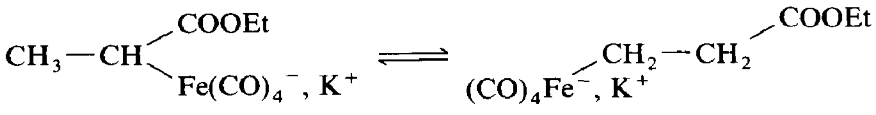
ing properties of the carboethoxy group which enhances the strength of the iron–carbon bond [16], a situation previously found for benzyl tetracarbonylferrates [17]. For such complexes, carbon monoxide insertions occur upon oxidation [17,18]. In fact, reaction of **3** with **1** in ethanol under a carbon monoxide atmosphere never gave detectable traces of ethyl 2-formyl propionate, whereas acyltetracarbonylferrates are known to yield aldehydes upon protonation [20]. It must also be noted that simple alkyltetracarbonylferrates, such as $CH_3CH_2Fe(CO)_4^-$, M^+ ($M = Et_4N$) give aldehydes upon reaction with **3** [21]. In the last case, the reaction has been shown to occur only by attack of $HFe(CO)_4^-$ on the coordinatively unsaturated acyl complex $CH_3CH_2C(O)Fe(CO)_3^-$, M^+.

The formation of diethyl 4-oxopimelate **7** was quite unexpected since, at least formally, this compound originates from an iron carbonyl complex in which the iron atom is linked to the β carbon atom of the organic ligand. Since **7** is formed throughout the reaction (see Table 2), the most plausible explanation involves an isomerisation of the alkyl ferrate **2** ($M = K$) in a way similar to that recently demonstrated to occur with neutral cobalt complexes (Scheme 5) in octane as solvent [22].

The addition of $NaHFe(CO)_4$ to **1** in THF has been reported to lead irreversibly to the alkyl ferrate **2** ($M = Na$) by a dissociative mechanism [3]. However, as discussed above, a different process is involved when the reaction is carried out in ethanol. Thus, it can be asked whether, in EtOH, the addition of **3** to **1** is reversible or not. A strong argument for the isomerisation of alkyl tetracarbonylferrates (eq. 7) may be found in the work of Takegami et al. [1] who have studied the reaction of $K_2Fe(CO)_4$ with ethyl α- and β-bromopropionates in EtOH. Their results showed that diethyl methylmalonate is the predominant product from both compounds (Scheme 6), which suggests that the equilibrium depicted in eq. 7 occurs and is strongly shifted to the left.



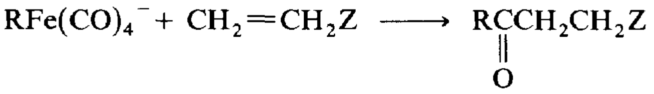
Scheme 6



$$\mathrm{CH_3{-}CH}\begin{matrix}\diagup\mathrm{COOEt}\\ \diagdown\mathrm{Fe(CO)_4^-,\ K^+}\end{matrix} \rightleftharpoons \begin{matrix}\mathrm{CH_2{-}CH_2{-}COOEt}\\ \diagup\\ \mathrm{(CO)_4Fe^-,\ K^+}\end{matrix} \qquad (7)$$

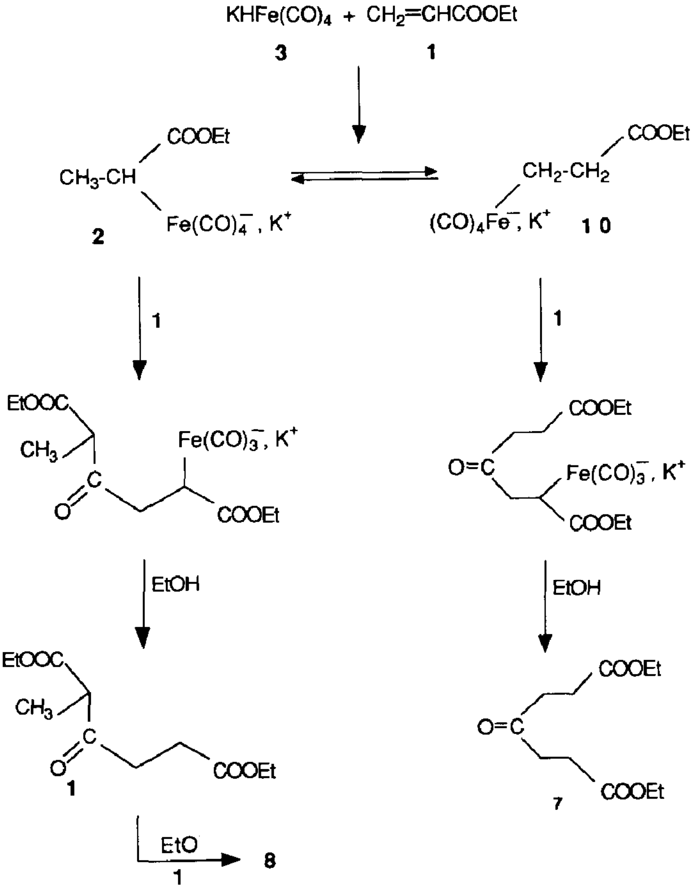
(2) **(10)**

Alkyl ferrates such as **10** are known to be protonated more rapidly than **2** [3]. Unlike their osmium analogues [23], hydrido(alkyl)tetracarbonyliron complexes are not stable, and reductive elimination occurs. Thus, the concentration of **10** in the reaction mixture may be low throughout the reaction. This may explain why the quenching of the reaction mixture with iodine never leads to more than 1–2% diethyl succinate. Also, **2** and **10** may react with the excess of **1**, as alkyltetracarbonylferrates generally do with Michael acceptors (eq. 8) [24]. With **2** and **10**, such reactions could account for the formation of **7** and **8** (Scheme 7).

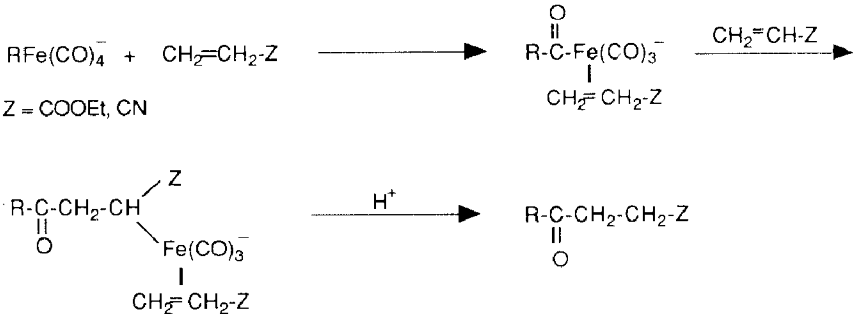


$$\mathrm{RFe(CO)_4^- + CH_2{=}CH_2Z \longrightarrow R\underset{\overset{\|}{O}}{C}CH_2CH_2Z} \qquad (8)$$

$(Z = COOEt, CN)$



Scheme 7



Scheme 8

The yield of diethyl 4-oxopimelate (**7**) (40%), is higher than that of **8** (5%). As the equilibrium depicted in eq. 7 is shifted to the left, it is not obvious why the yield of **8** is lower than that of **7**. An explanation may lie in the fact that the hydroacylation of Michael acceptors through reactions with organotetracarbonyl ferrates does not proceed by ligand exchange, but by two sequential migratory insertion reactions [24] (Scheme 8). As previously noted, carbon monoxide insertion into the iron-carbon bond of **2** is difficult. The reaction of **1** with **2** is thus slower than that with **10**, thus explaining the difference in yields (**7** > **8**). Furthermore, the higher reactivity of **10** also accounts for the fact that quenching the reaction mixture with iodine always leads to a very high **6**/diethyl succinate ratio.

A search of the literature showed that the synthesis of dialkyl 4-oxopimelate is often tedious [25]. To the best of our knowledge, the most practical way of preparing these compounds from the corresponding acrylates involves reaction with a $Co_2(CO)_8$-diphos system under 100 bar carbon monoxide at 135 °C in water-dioxane mixtures. Yields of up to 94%, relative to water, have been reported, which corresponds to 22% relative to acrylate (a large acrylate/cobalt ratio is necessary) [26]. A rhodium-catalyzed synthesis has recently been disclosed [27] which is operative under 100 bar at 180 °C (495% relative to Rh). Thus, the formation of diethyl 4-oxopimelate discovered in this study may be worth further study as a new way to such compounds.

Conclusion

The reaction of $KHFe(CO)_4$ with an excess of ethyl acrylate in ethanol has been shown to be much more complicated than had previously been suggested.

It has been found for the first time that $KHFe(CO)_4$ provides a 270% yield (/iron) reduction of ethyl acrylate to ethyl propionate, independent of whether the atmosphere is argon or carbon monoxide. This reaction involves in situ protonation of the intermediate alkyltetracarbonylferrates **2** or **10** to give ethyl propionate and an unstable $Fe(CO)_4$ moiety which reacts with ethyl acrylate to generate the $Fe(CO)_4$(acrylate) complex. Further reaction of this complex with potassium ethoxide in the presence of an excess of ethyl acrylate leads to ethyl propionate in a pseudocatalytic manner.

Whereas the addition of $HFe(CO)_4^-$ to ethyl acrylate in THF is regioselective and irreversible, the situation and the mechanism are different when ethanol is used as solvent. Indeed, in ethanol, the reaction is not inhibited by a carbon monoxide atmosphere, suggesting a radical or concerted mechanism rather than a dissociative process. The addition is regioselective, but reversible, leading first to **2**, which is slowly isomerised to **10**. As **10** is much more reactive than **2** towards both proton sources and ethyl acrylate, its concentration is low throughout the reaction. Thus, quenching the reaction medium with iodine always leads to a very high diethyl methylmalonate/diethyl succinate ratio.

Lastly, this reaction has been found to be worth studying as a new method for the synthesis of diethyl 4-oxopimelate.

Experimental

A. General

All experiments were carried out under a well-ventilated hood. Manipulations of air-sensitive iron complexes were performed under an argon atmosphere using standard Schlenck tube techniques. For runs under pressure, a 80 ml glass-lined stainless steel (316 STI) autoclave, equipped with a magnetic stir bar was used. Absolute ethanol (Prolabo-Normapur), $Fe(CO)_5$ (Aldrich), ethyl acrylate (Aldrich, 99%) and KOH (Prolabo, 85%) were used without further purification. Argon U (L'Air Liquide) and carbon monoxide (N20, L'Air Liquide) were used.

IR spectra were obtained with a Perkin–Elmer 597 spectrometer using CaF_2 (0.05 mm) windows. ^1H NMR spectra were obtained using Bruker WH 90 and WH 250 MHz spectrometers. ^{13}C NMR spectra were obtained with a Bruker WH 250 MHz spectrometer.

Reactions were monitored by GC analysis on a Girdel 330 or an Intersmat IGC 121 gas chromatograph (flame ionization detectors) equipped with a 50 m capillary column (OV1, on-column injector), or a 1.5 m SE 30 (10%) column. In all cases, peak areas were determined using a Spectra Physics SP 4290 computing integrator. Mass spectra were recorded on a Nermag R10-10A spectrometer (chemical ionisation-NH_3-source temperature: 100 ° C).

B. Preparation of $KHFe(CO)_4$

A solution of KOH (22 mmol) in ethanol (50 ml) was deaerated with argon for 0.5 h. $Fe(CO)_5$ (1.5 ml, 11 mmol) was then added and the mixture allowed to react for 0.5 h at room temperature. The IR spectrum exhibited two main bands at 1920 (sh) and 1900 (s) cm^{-1}.

C. General procedure

Ethyl acrylate (11 or 66 mmol, see text) and decane (16 mmol) (GC internal standard) in absolute ethanol (10 ml) were added to the $KHFe(CO)_4$ solution and the reaction mixture was heated to 70 ° C in an oil bath. For reactions conducted under CO, the reaction flask was previously purged with CO and connected to a gas buret filled with CO (1 atm). Small aliquots (1 ml) were removed periodically through a septum cap. Half of the aliquot was added to 0.5 ml of a fresly prepared ethanolic solution of acetic acid (~ 0.5 *M*). The other half was added to 0.5 ml of a solution of iodine in absolute ethanol. Both solutions were then analysed by GC (capillary OV1 or SE 30 column, respectively).

D. Isolation of 2 ($M^+ = PPN^+$)

An ethanolic solution of **3**, prepared as described above, was filtered under argon (to remove the potassium bicarbonate). The solution was then allowed to react with a slight excess of **1** (12 mmol) for 6.5 h at 35 °C under carbon monoxide (1 atm). PPNCl was then added and the reaction mixture stirred for 1 h at 35 °C and then for 20 h at room temperature. The solution was then placed in a refrigerator at −20 °C until orange crystals separated. Classical work-up gave **2** in a very pure form (20%). Spectroscopic data on **2** are given in Table 1.

E. Isolation of 7 and 8

At the end of the reaction (see Table 2), the reaction mixture was treated with dilute HCl until pH 7, extracted with diethyl ether, washed several times with water, dried over sodium sulfate and evaporated. Liquid chromatography through a silica column (hexane/diethyl ether mixtures as eluents) gave **7** and **8**.

The ester **7** was identified by comparison (IR, ^{1}H, ^{13}C NMR and GC-MS) with a commercial sample of diethyl 4-oxopimelate (Aldrich) ^{13}C NMR ($CDCl_3$; 62.8 MHz): δ 206.5 (s, CO); 172.2 (s, *C*OOEt), 60.1 (t, ^1J(CH) 147 Hz, OCH_2CH_3); 36.6 (t, ^1J(CH) 127 Hz, $C(O)CH_2CH_2CO_2Et$); 27.6 (t, ^1J(CH) 130 Hz, CH_2COOEt); 13.7 (q, ^1J(CH) 127 Hz, CH_2CH_3).

8: GC/MS, CI, gas reactant NH_3 (1 torr), pseudomolecular ion source: MH^+ $m/z = 331$; $MNH_4{}^+$ $m/z = 348$, $m/z = 285$, IR (νC=O) 1740 (br) cm^{-1}, ^{1}H NMR ($CDCl_3$, 250 MHz): δ 4.19 (q); 4.11 (q); 4.10 (q); 2.76–2.82 (m); 2.52–2.59 (m); 2.09–2.36 (m); 1.37 (s); 1.20–1.29 (m). ^{13}C NMR ($CDCl_3$, 62.8 MHz): 205.7 (s, CO); 172.8 (s, COOEt); 172.4 (s, *C*OOEt); 172.33 (s, *C*OOEt), 61.5 (t, ^1J(CH) 147 Hz, OCH_2CH_3); 60.6 (t, ^1J(CH) 147 Hz, OCH_2CH_3); 60.5 (t, ^1J(CH) 147 Hz, OCH_2CH_3); 58.4 (s, quaternary C); 33.2 (t, ^1J(CH) 127 Hz, $C(O)CH_2CH_2COOEt$); 29.9 (t, ^1J(CH) 133 Hz, CH_2COOEt); 29.5 (t, ^1J(CH) 130 Hz, CH_2COOEt); 28.1 (t, ^1J(CH) 126 Hz, CH_2CH_2COOEt); 19.1 (q, ^1J(CH) 130 Hz, CH_3); 14.1 (q, ^1J(CH) 127 Hz, two $CO_2CH_2CH_3$); 14.0 (q, ^1J(CH) 127 Hz, $CO_2CH_2CH_3$).

F. Preparation of 9

The complex **9** was prepared by a standard procedure [13]. $Fe_2(CO)_9$ (12.9 g) and ethyl acrylate (4.2 ml) were heated for 2 h at 45 °C in 50 ml benzene. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica, in order to remove all traces of $Fe_3(CO)_{12}$. **9** was obtained as a yellow liquid (85%).

IR(EtOH) ν(CO): 2099, 2025, 2001, 1991 cm^{-1}; ν(COOEt): 1707, 1684 cm^{-1}.

G. Reactivity of 9

A solution of **9** (8 mmol) and ethyl acrylate (31 mmol) in ethanol (45 ml) was heated under argon for 30 h at 70 °C in the presence of either $KHCO_3$ (8 mmol) or K_2CO_3 (8 mmol). The reaction was monitored by the GC analysis (with decane as the internal standard) of small aliquots.

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