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THE REACTION OF CARBONYLHYDRIDOFERRATE(O) IN APROTIC SOLVENTS. I. HYDROACYLATION OF α,β-UNSATURATED CARBOXYLIC ESTERS

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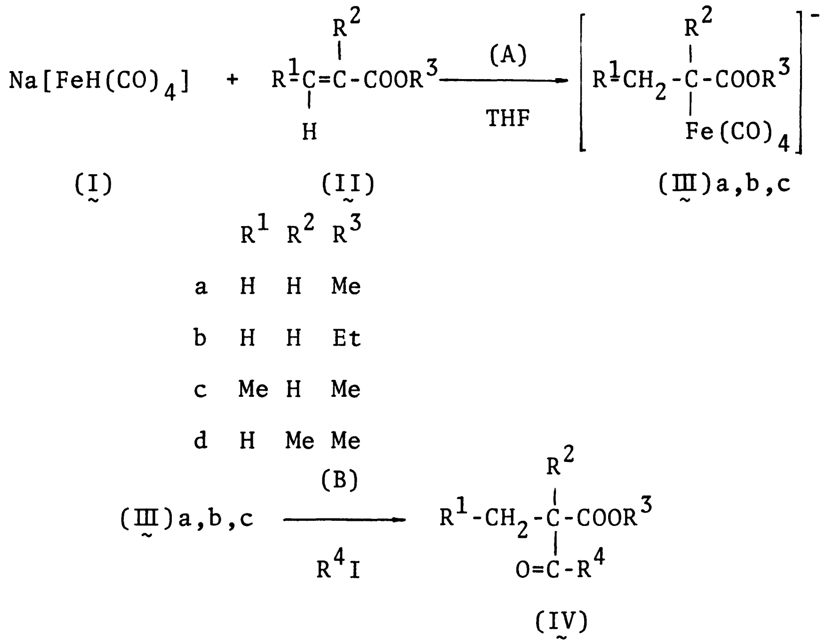
α,β-Unsaturated carboxylic esters selectively insert into the hydrogen-iron bond of $[FeH(CO)_4]^-$ in an aprotic solvent under an ambient condition to give an alkyl-iron complex, which gives a hydroacylated product by treatment with alkyl iodide.

The reaction of tetracarbonylhydridoferrate(0), $[FeH(CO)_4]^-$ (I), which is recently proposed to be the catalytic species in Reppe's hydroxymethylation,[1] with unsaturated compounds such as olefin has been studied.[2] However, almost all of these reactions were carried out in protic solvents such as alcohol and/or water, and the hydrogen transfer occurred too readily to isolate the reaction intermediate.

In this letter we wish to report the hydroacylation[3] of α,β-unsaturated carboxylic ester (II) using the ferrate (I) and alkyl iodides in aprotic solvents under an ambient condition. α,β-Unsaturated carboxylic esters (II) selectively insert into the hydrogen-iron bond of (I) to give alkyl-carbonylferrate (III), which can be isolated as a bis(triphenylphosphine)iminium salt. The complex (III) is converted into a hydroacylated compound by treating with alkyl iodide[4] (Scheme-1).

Scheme-1



The typical results of the hydroacylation are shown in Table-1.

TABLE-1. HYDROACYLATION OF α,β-UNSATURATED CARBOXYLIC ESTERS.

	R^1-CH=C(R^2)-COOR^3 R^1	R^2	R^3	R^4I	Temp(°C) (A)*1	(B)	Solvent (A)	(B)	Time (hr) (A)	(B)	Product	Yield*3 (%)
a	H	H	Me	EtI	20	30	THF	THF-NMP*2 2 : 1	1	48	2-methyl-3-oxovalerate	80
b	H	H	Et	MeI	30	30	THF	THF	2.5	14	2-methyl-3-oxobutyrate	74
c	Me	H	Me	MeI	50	30	THF	THF	5	14	2-ethyl-3-oxobutyrate	43
c	Me	H	Me	MeI	30	30	THF	THF-NMP 2 : 1	15	30	2-ethyl-3-oxobutyrate	67
d	H	Me	Me	—	50	—	THF	—	24		no reaction	

*1. (A) and (B) mean the reactions (A) and (B) in Scheme-1, respectively.

*2. N-Methyl-2-pyrrolidone.

*3. Yields, based on $[FeH(CO)_4]^-$, were determined by gas chromatography.

The reaction procedure will be illustrated by the synthesis of ethyl 2-methyl-3-oxobutyrate. Ethyl acrylate (IIb) (5.5 mmol) was added to $[FeH(CO)_4]^-$ (I) (5.5 mmol) in THF[5] (38 ml) at 30°C under an argon atmosphere and agitated for 1 hr.[6] Then the reaction mixture was treated with 11 mmol of methyl iodide to give selectively ethyl 2-methyl-3-oxobutyrate in a 74% yield. The yield was improved by the addition of 19 ml of N-methyl-2-pyrrolidone to the solution of (III).[4] In all cases, acylation selectively occurred on the α-position of the ester group.

The insertion of (II) into hydrogen-iron bond of (I) is dramatically affected by the atmospheres; under a carbon monoxide atmosphere the insertion reaction is practically suppressed at room temperature in contrast to that under an argon atmosphere. This effect may be due to the following equilibrium,[1]

$$[FeH(CO)_4]^- \rightleftharpoons [FeH(CO)_3]^- + CO$$

and the tricarbonylferrate appears to be a real active species in this reaction. Analogous effect has been observed in the reaction of tetracarbonylhydridocobalt (I).[7] The insertion reaction is also affected by the substituent on the α-position of the ester (R^2). Methyl methacrylate (IId) does not react with (I) even at 50°C. This may attribute to the steric hindrance of the methyl group.

The complex (IIIa) was isolated[8] from the reaction mixture as a bis(triphenylphosphine)iminium salt[9] (Yield 37%), which supports the reaction scheme 1. $[(P\phi_3)_2N]^+ \left[\begin{array}{l} H_3C\text{-}CHCOOMe \\ \quad\quad Fe(CO)_4 \end{array} \right]^-$; m p (under argon) 114-116°C dec. Anal. Calcd. for $C_{44}H_{37}O_6NP_2Fe$: C, 66.59; H, 4.70; N, 1.77%. Found: C, 66.29; H, 4.59; N, 1.58%. IR (KBr disk): νCO 1998(m), 1901(s), 1887(s), νCO_{ester} 1667(m) cm^{-1}. PMR (220 MHz Acetone d_6): τ 6.6(s, 3H), 7.6(q, 1H, J=7 Hz), 8.6(d, 3H, J=7 Hz)ppm. Further organic syntheses using (I) in aprotic solvent are in progress.

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A. Misono, Y. Uchida, K. Tamai, and M. Hidai, *ibid.*, 40, 931 (1967), and the references therein.

3) During this study, hydroacylation using cobalt and rhodium hydride complexes has been reported; J. Schwartz and J. B. Cannon, *J. Amer. Chem. Soc.*, 96, 4721 (1974).

4) Ketone syntheses by the reaction of alkyl or acyl halide with $Na_2[Fe(CO)_4]$ have been reported; J. P. Collman, S. R. Winter, and D. R. Clark, *J. Amer. Chem. Soc.*, 94, 1788 (1972).

5) $[FeH(CO)_4]^-$ in THF was prepared by the protonation of $Na_2[Fe(CO)_4]$ in THF with an equivalent mole of acetic acid.

$$Na_2[Fe(CO)_4] + CH_3COOH \xrightarrow{THF} Na[FeH(CO)_4] + CH_3COONa$$

From this solution $[FeH(CO)_4]^-$ was quantitatively isolated as a bis(triphenylphosphine)iminium salt; Anal: Calcd. for $C_{40}H_{31}O_4NP_2Fe$: C, 67.91; H, 4.21, N, 1.98%. Found: C, 67.14; H, 4.61; N, 2.00%. IR (KBr disk): νCO 1995(m), 1904(s), 1880(s) cm^{-1}. PMR (60 MHz, CH_2Cl_2): τ 18.9 (H-Fe) ppm.

6) The ir spectrum of the reaction solution showed that the carbonyl band of ethyl acrylate completely disappeared and the new absorption at 1640 cm^{-1} appeared.

7) R. F. Heck and D. S. Breslow, *J. Amer. Chem. Soc.*, 83, 4023 (1961). M. Orchin and W. Rupilius, *Catalysis Rev.*, 6, 85 (1972).

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