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SELECTIVE TRIMERIZATION OF ALIPHATIC ALDEHYDES CATALYZED BY POLYNUCLEAR CARBONYLFERRATES

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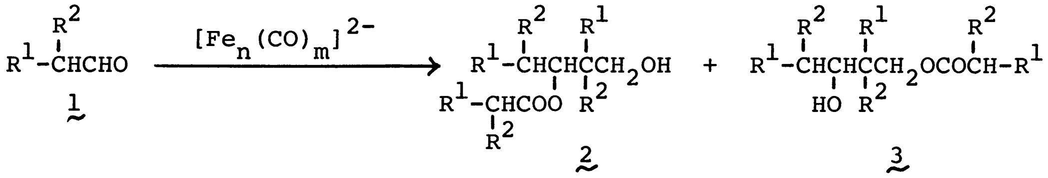
Aliphatic aldehydes undergo a catalytic trimerization to give 1,3-diol monoesters upon treatment with $Fe_3(CO)_{12}$ in pyridine or with $Fe_3(CO)_{12}$-pyridine N-oxide in benzene. Polynuclear carbonylferrates serve as catalyst for this transformation.

Mononuclear carbonylferrates such as $[Fe(CO)_4]^{2-}$ and $[CpFe(CO)_2]^-$ induce a variety of organic transformations.[1,2] For example, $[Fe(CO)_4]^{2-}$ catalytically promotes a dismutation of aromatic aldehydes ArCHO to esters $ArCOOCH_2Ar$.[3] Aliphatic aldehydes undergo the aldol condensation upon treatment with $[Fe(CO)_4]^{2-}$ or $[HFe(CO)_4]^-$.[3,4] However, little attention has been focused on the utility of polynuclear carbonylferrates in organic synthesis. Previously, we have shown that octacarbonyl diferrate, $[Fe_2(CO)_8]^{2-}$, induces a reductive dimerization of aromatic aldehydes to give 1,2-diaryl-1,2-ethanediols in a stoichiometric manner.[5] We now report that a certain kind of polynuclear carbonylferrates catalytically promotes a trimerization of aliphatic aldehydes to give 1,3-diol monoesters.



a: R^1=Et, R^2=H; b: R^1=i-Pr, R^2=H; c: R^1=Me, R^2=Me; d: R^1=n-Pr, R^2=Me;

A solution of $Fe_3(CO)_{12}$ (0.41 mmol) in pyridine (3 ml) was degassed by three freeze-pump-thaw cycles and heated at 80°C for 1.5 h. Butanal (1a, 30 mmol) was then added and the mixture was heated at 80°C for 15 h. After removal of the solvent, the residue was chromatographed on silica gel. Elution with benzene-ethyl acetate (4:1) gave a mixture of 3-butyryloxy-2-ethyl-1-hexanol (2a) and 1-butyryloxy-2-ethyl-3-hexanol (3a) in a 3:7 ratio. The total yield of 2a and 3a was 93% based on 1a and 2300% based on $Fe_3(CO)_{12}$ used.

Similar treatment of aldehydes 1b-d gave the corresponding 1,3-diol monoesters

Table 1. Reaction of Aliphatic Aldehydes with $Fe_3(CO)_{12}$ in Pyridine

Run No		Aldehyde		Molar ratio of	1,3-Diol monoesters	
		R^1	R^2	**1** $/Fe_3(CO)_{12}$	Total yield (%)$^{a)}$	Ratio of **2** / **3**$^{b)}$
1	**1a**	C_2H_5	H	73	93 (2300)	3 / 7
2	**1b**	$(CH_3)_2CH$	H	50	50 (830)	4 / 6
3	**1c**	CH_3	CH_3	50	64 (1100)	6 / 4
4	**1d**	$CH_3CH_2CH_2$	CH_3	50	44 (730)	6 / 4
5	**1e**	CH_3CH_2	CH_3CH_2	10	no reaction	
6	**1f**	$(CH_3)_3CCHO$		10	no reaction	

a) Isolated yields based on aldehydes used. Figures in parentheses indicate the yields based on $Fe_3(CO)_{12}$ used. b) The proportion of **3** in the reaction mixtures increased with prolonging the reaction time.

Table 2. Reaction of Aliphatic Aldehydes with $Fe_3(CO)_{12}$-Pyridine N-oxide in benzene$^{a)}$

Run No		Aldehyde		Molar ratio of	1,3-Diol monoesters	
		R^1	R^2	**1** $/Fe_3(CO)_{12}$	Total yield (%)$^{b)}$	Ratio of **2** / **3**$^{c)}$
7	**1a**	C_2H_5	H	300	91 (9100)	9 / 1
8	**1b**	$(CH_3)_2CH$	H	300	33 (3300)	8 / 2
9	**1c**	CH_3	CH_3	300	83 (8300)	9 / 1
10	**1d**	$CH_3CH_2CH_2$	CH_3	300	12 (1200)	8 / 2
11	**1e**	CH_3CH_2	CH_3CH_2	10	no reaction	
12	**1f**	$(CH_3)_3CCHO$		10	no reaction	

a) After heating a solution of $Fe_3(CO)_{12}$ (0.2 mmol) and pyridine N-oxide (0.05 mmol) in benzene (2 ml) at 80°C for 40 min, an aldehyde was added, and then the resulting mixture was heated at 80°C for 15 h under degassed conditions. b) Isolated yields based on aldehydes used. Figures in parentheses indicate the yields based on $Fe_3(CO)_{12}$ used. c) The proportion of **3** in the reaction mixtures increased with prolonging the reaction time.

2b-d and **3b-d**. The results are given in Table 1. The same esters **2a-d** and **3a-d** were also obtained by treating the aldehydes **1a-d** with the reagent prepared from $Fe_3(CO)_{12}$ and pyridine N-oxide (PyNO) in benzene (Table 2). The reactions were catalytic with respect to the Fe species. However, these reactions did not occur when an aldehyde such as **1f** which has no α-hydrogen and a sterically hindered aldehyde such as **1e** were used as substrates. Structure of the products were assigned from their analytical and spectral data.$^{6)}$

To obtain information regarding the nature of active catalyst in these reactions, the reaction of **1a** with several carbonylferrates were studied. The results are shown in Table 3. It must be noted here that $Fe_3(CO)_{12}$ is converted into the diferrate species $[Fe_2(CO)_8]^{2-}$ upon heating at 80°C for 1.5 h in pyridine.$^{5)}$ Furthermore, it was found that treatment of $Fe_3(CO)_{12}$ with a small amount of PyNO in benzene affords polynuclear carbonylferrates which contain $[Fe_2(CO)_8]^{2-}$ as a major constituent.$^{7,8)}$

Table 3. Reaction of Butanal (1a) with Carbonylferrates[a)]

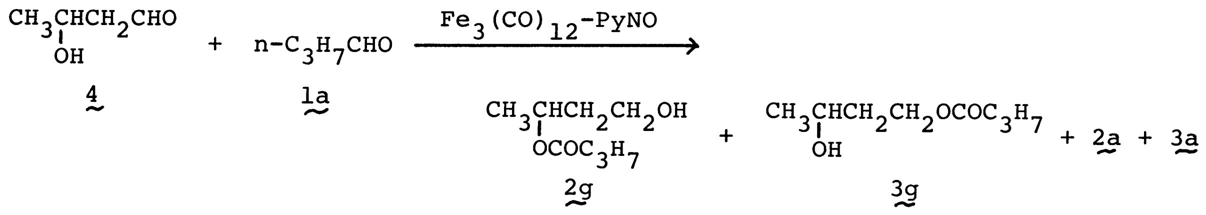
Run No	Butanal (mmol)	Iron Carbonyl (mmol)	Yield of 2a + 3a (%)[b)]	Ratio of 2a / 3a[c)]	Aldol-product[d)] Yield (%)[b)]
13	30	$Fe_3(CO)_{12}$ (0.40) + PyNO (0.10)	95	9 / 1	trace
14	30	$Et_3NH[HFe_3(CO)_{11}]$ (0.44)	89	3 / 7	trace
15	20	$Na_2Fe_2(CO)_8$ (5.0)	55	6 / 4	8
16	40	$Na_2Fe(CO)_4$ (0.80)	15	5 / 5	50[e)]
	13	$Na_2Fe(CO)_4$ (11)	-	-	70[3)]

a) A mixture of butanal and iron complex in benzene was heated at 80°C for 15 h under degassed conditions. In the case of Run 13, a solution of $Fe_3(CO)_{12}$ and pyridine N-oxide (PyNO) was heated at 80°C for 40 min before butanal was added. In the cases of Runs 15 and 16, the reaction was conducted in THF at 60°C for 15 h. b) Isolated yields based on butanal used. c) The proportion of 3 in the reaction mixtures increased with prolonging the reaction time. d) A mixture of 2-ethyl-2-hexenal and 2-ethyl-hexanal was obtained. e) Besides the products cited in this table, a small amount of unidentified product was also obtained.

These results suggest that the ferrate complexes have the following reactivity features. Firstly, a certain kind of polynuclear carbonylferrates such as $[Fe_2(CO)_8]^{2-}$ and $[HFe_3(CO)_{11}]^-$ serves as catalyst for the trimerization of aliphatic aldehydes. Secondary, mononuclear carbonylferrate such as $[Fe(CO)_4]^{2-}$ preferentially promotes the aldol condensation of aldehydes.[3,4)]

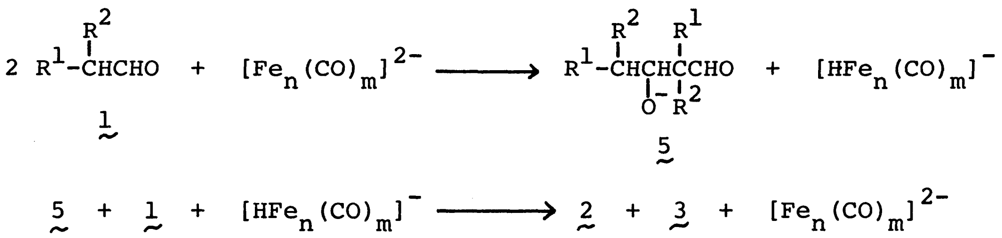
The trimerization of aliphatic aldehydes to 1,3-diol monoesters is also effected by some sorts of metal alkoxides and phenoxides such as $Ca(OC_2H_5)_2$,[9)] $Mg[Al(OC_2H_5)_4]_2$,[9)] C_6H_5OMgX,[10)] and $(CH_3)_3C_6H_2OMgX$.[10)] However, in these reactions, significant amounts of esters of the type $RCOOCH_2R$ derived by a dismutation of aldehydes are usually produced as by-products, together with significant amounts of aldol-condensation products. On the other hand, in the case of the polynuclear-ferrate-catalyzed reaction, the 1,3-diol monoesters are formed with high selectivity.

The mechanistic implication of this trimerization was obtained from the following observations. A mixture of 3-hydroxy-butanal (4) (30 mmol), 1a (15 mmol) and $Fe_3(CO)_{12}$ (1.1 mmol)-PyNO (0.27 mmol) in benzene (3 ml) was heated at 80°C for 15 h. Work-up of the resulting mixture gave a 8:2 mixture of the cross-condensed products 2g and 3g (910% yield based on $Fe_3(CO)_{12}$ used), together with 2a and 3a (45% yield based on $Fe_3(CO)_{12}$ used) which were produced by the trimerization of 1a.



$$\underset{\mathbf{4}}{\underset{\mid\;\;\;\;\;\;\;}{CH_3CHCH_2CHO}_{\!\!\!\!OH}} + \underset{\mathbf{1a}}{n\text{-}C_3H_7CHO} \xrightarrow{Fe_3(CO)_{12}\text{-PyNO}} \underset{\mathbf{2g}}{\underset{OCOC_3H_7}{CH_3CHCH_2CH_2OH}} + \underset{\mathbf{3g}}{\underset{OH}{CH_3CHCH_2CH_2OCOC_3H_7}} + \mathbf{2a} + \mathbf{3a}$$

The possible reaction pathways for the trimerization of aldehydes are outlined in Scheme 1. The hydridoferrate $[HFe_n(CO)_m]^-$ may also act as catalyst for this reaction. The detailed experiments suggested that 3-acyloxy-isomers **2** are initially produced from **5**, and then **2** isomerize to 1-acyloxy-isomers **3**. The catalytic ability of polynuclear carbonylferrates in this reaction is possibly attributed to their bifunctional activity: the basicity of the ferrates promotes the aldol-condensation of **1** to **5**, and their hydride-transfer ability mediates the dismutation reaction between **1** and **5** to form **2** and **3**.



Scheme 1

References

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6) As an example, the ^1H-NMR($CDCl_3$) data of **2a** and **3a** are shown: **2a**; δ0.8-1.1(9H, m), 1.1-1.8(9H, m), 2.2(2H, t), 3.4(2H, d), and 5.0(1H, m). **3a**; δ0.8-1.1(9H, m), 1.1-1.8(9H, m), 2.2(2H, t), 3.5(1H, m), and 4.1(2H, d). The relative ratio of **2a**/**3a** was determined from the NMR spectrum of the reaction mixture.
7) A solution of $Fe_3(CO)_{12}$ (1.0 mmol) and PyNO (0.3 mmol) in benzene was heated at 80°C for 30 min. The mixture was treated with $[(Ph_3P)_2N]Cl$ (2 mmol) in CH_2Cl_2, giving the salt $[(Ph_3P)_2N]_2[Fe_2(CO)_8]$ in a 68% yield. Found: C, 67.03; H, 4.10; N, 1.87%. Calcd. for $C_{80}H_{60}Fe_2N_2O_8P_4$: C, 68.00; H, 4.28; N, 1.98%. IR(KBr) 1905 cm^{-1}(m), 1866 cm^{-1}(s).
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