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The Reaction of Disodium Tetracarbonylferrate(−II) with Aldehydes[1]

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Disodium tetracarbonylferrate (−II) is an efficient catalyst for the dismutation of aromatic aldehydes to esters, $2RCHO \rightarrow RCOOCH_2R$. Aliphatic ones give aldol-condensation products upon treatment with the ferrate. A successive reaction of the ferrate with an aldehyde, RCHO, and then with alkyl iodide, R'I, gives an ester, $R'COOCH_2R$, after protonation. The mechanisms of these reactions are discussed.

Disodium tetracarbonylferrate(−II) (**1**) is known to be a selective reagent for organic syntheses. For example, using this reagent, alkyl halides or carboxylic acid derivatives are selectively converted into aldehydes[2–5] or ketones,[6,7] and enol esters are derived from β-oxoalkyl halides.[8]

Although the reactions of alkyl halides, tosylates, or carboxylic acid derivatives with **1** have been studied hitherto, little attention has been paid to the reaction of **1** with carbonyl compounds. This report will deal with the reaction of **1** with aldehydes.

Results and Discussion

Certain aldehydes react with **1** under mild conditions to give an ester; two aldehyde groups are transformed into the corresponding alkoxyl and carboxyl functions, existing in combination as an ester. These reactions proceed by means of a catalytic amount of

$$2RCHO \xrightarrow{(1)} RCOOCH_2R$$

1. When benzaldehyde (100 mmol) was treated with **1** (3 mmol) in tetrahydrofuran at 25 °C for 40 h under an argon atmosphere, an essentially complete convertion of the aldehyde was observed and benzyl benzoate was obtained in a 95% yield. Under similar conditions, *p*-tolualdehyde, *p*-chlorobenzaldehyde, and α-naphthaldehyde gave the corresponding esters. *p*-Anisaldehyde scarcely reacted with **1** at 25 °C, but gave the *p*-methoxybenzyl *p*-methoxybenzoate ester at 60 °C. The by-products obtained in these reactions were small amounts of alcohols such as benzyl alcohol (less than 3%). Aliphatic aldehydes and furfural also reacted with **1** under identical conditions, but the corresponding esters were not obtained. Furfural gave only tarry materials upon treatment with **1**. The treatment of aliphatic aldehydes such as *n*-butyraldehyde with an equimolar amount of **1** gave aldol condensates and then hydrogenated products, such as 2-ethyl-2-hexenal and 2-ethylhexanal. The formation of these products is due to the basicity of **1**, $[Fe(CO)_4]^{2-}$ [9] and the reducing ability of $[FeH(CO)_4]^-$ [10] which transforms α,β-unsaturated carbonyl compounds into saturated ones.[11] The results are summarized in Table 1. The conditions were not optimized for these reactions. These reactions are scarcely affected by the atmosphere; no remarkable difference was detected in the reaction rates under a carbon monoxide atmosphere compared with that under an argon atmosphere.

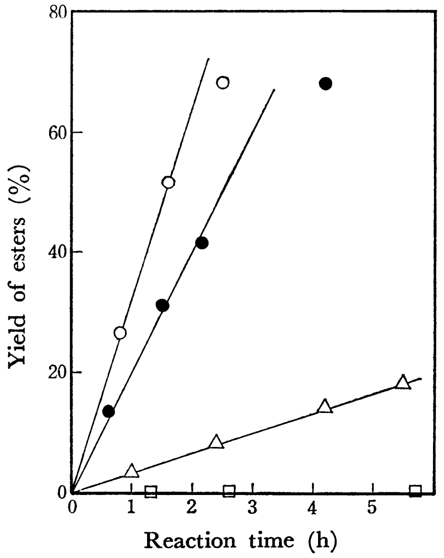


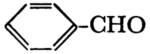
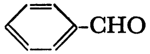
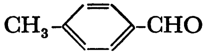
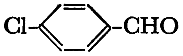
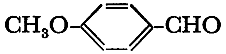
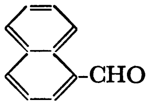
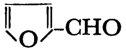
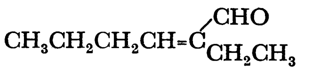
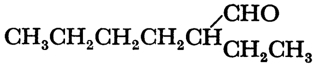
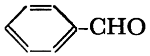
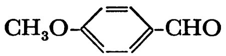
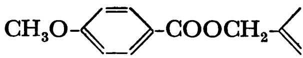
Fig. 1. Yield of ester *vs.* time plots for the reaction of $Na_2Fe(CO)_4$ with aldehydes (in THF, at 25 °C, under argon).
○ : *p*-Chlorobenzaldehyde, ● : benzaldehyde, △ : *p*-tolualdehyde, □ : *p*-anisaldehyde.

In the reactions of *p*-substituted benzaldehydes with **1**, there is a remarkable influence of the substituents on the relative reaction rates. The yields of esters *vs.* time plots for the reaction of **1** with the substituted benzaldehydes are shown in Fig. 1. The apparent order of their reactivities was as follows: $p\text{-}ClC_6H_4CHO > C_6H_5CHO > p\text{-}CH_3C_6H_4CHO > p\text{-}CH_3OC_6H_4CHO$. The reactivity decreases with an increase in the electron-releasing property of the substituents. This suggests that the reaction is influenced by the electron density on the carbonyl carbon of the aldehydes which the ferrate (**1**) attacks nucleophilically.

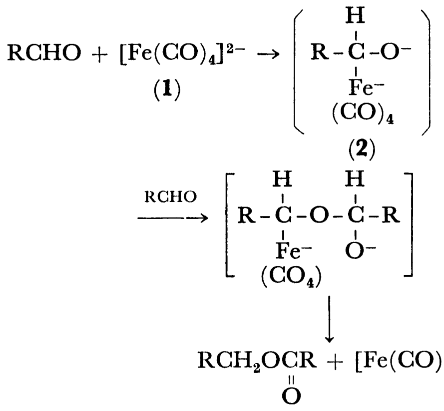
When an equimolar mixture of benzaldehyde (50 mmol) and *p*-anisaldehyde (50 mmol) was stirred with **1** (3 mmol) at 25 °C, 17 mmol of benzyl benzoate and 11 mmol of benzyl *p*-methoxybenzoate were obtained, but no *p*-methoxybenzyl *p*-methoxybenzoate and *p*-methoxybenzyl benzoate were produced. This shows that *p*-anisaldehyde can react as only an acid component even at 25 °C, though alone it scarcely reacts with **1** at this temperature (Exp. 5).

As the reaction scheme, the following one is considered (Scheme 1). First, the ferrate (**1**) attacks the carbonyl carbon of the aldehyde nucleophilically to give an adduct (**2**). The addition of the second aldehyde to **2** is followed by the loss of the ferrate

TABLE 1. REACTION OF ALDEHYDES WITH $Na_2Fe(CO)_4$

Exp. No.	Aldehyde (mmol)	$Na_2Fe(CO)_4$ (mmol)	Reaction conditions			Product	Yield (%)[a]
			Temp (°C)	Time (h)	Solvent		
1	 (100)	3	25	40	THF		95
2	 (100)	3	25	20	THF-NMP[b)] 1 : 1		92
3	 (100)	3	25	50	THF		73
4	 (100)	3	25	20	THF		90
5	 (100)	3	25	50	THF	—[c)]	—
6	 (100)	3	60	20	THF		76
7	 (100)	3	25	40	THF		72
8	 (30)	6	25	20	THF	—[d)]	—
9	$CH_3CH_2CH_2CHO$ (13)	11	25	3	THF	 $CH_3CH_2CH_2CH{=}C(CHO)CH_2CH_3$	38
						 $CH_3CH_2CH_2CH_2CH(CHO)CH_2CH_3$	32
10	 (50)	3	25	40	THF		(17 mmol)
	 (50)						(11 mmol)

a) Based on the amount of aldehydes. b) *N*-Methylpyrrolidone. c) The remainder consisted mainly of the starting material. d) Tarry materials were obtained.



Scheme 1.

to give the esters. This scheme is roughly the same as that of the well-known variations of the base-induced dismutation of aldehydes, *e.g.*, catalyzed by the RO⁻ alkoxide.[12] In the base-catalysed dismutation of aldehydes, the view that the first step of the reaction proceeds by an initial coordination of the base with the aldehyde carbonyl group is supported by the investigations of the effect of substituents upon the rate of the reaction.[12]

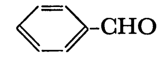
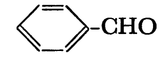
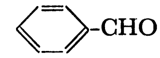
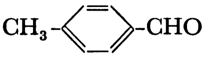
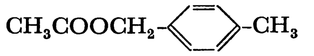
The formation of benzyl *p*-methoxybenzoate (Exp. 10) implies that *p*-anisaldehyde is able to react with the adduct (**2**), as a second aldehyde, though it does not form an adduct (**2**) upon treatment with **1** at 25 °C.

After **1** had been stirred with an equimolar amount of an aldehyde (R^1CHO) in tetrahydrofuran at 25 °C for 5 h, an excess of alkyl iodide (R^2I) was added and the reaction mixture was stirred for an additional 5 h. After the treatment of the mixture with acetic acid and a usual workup, a second ester, $R^2COOCH_2R^1$, was obtained besides the $R^1COOCH_2R^1$ ester. The

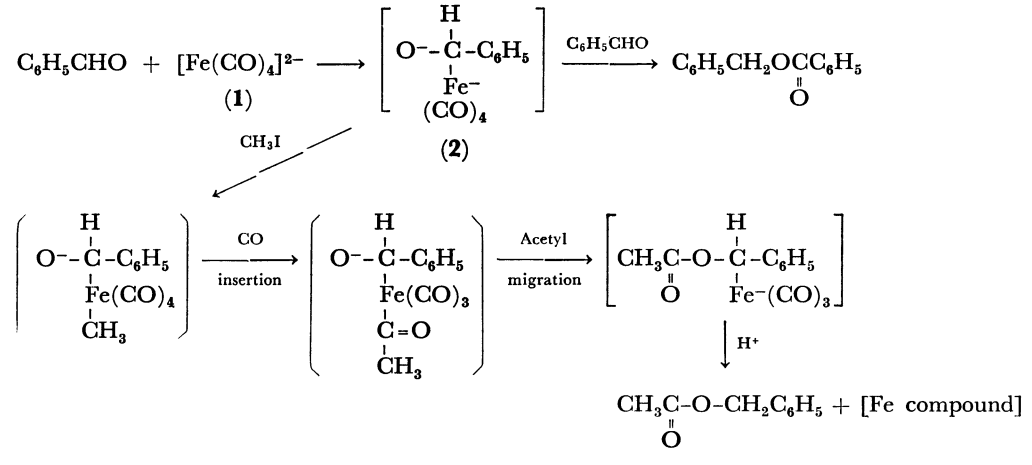
$$R^1CHO \xrightarrow[\text{ii) } R^2I \text{ iii) } H^+]{\text{i) (1)}} R^2COOCH_2R^1 + R^1COOCH_2R^1$$

results are listed in Table 2. The acetyl and propionyl groups of the esters ($R^2COOCH_2R^1$) appear to be from methyl or ethyl iodide, and the ferrate

Table 2. Successive reactions of $Na_2Fe(CO)_4$ with aldehyde and with alkyl iodide[a)]

Exp. No.	Aldehyde (mmol)	RI (mmol)	Reaction conditions Temp (°C)	Time (h) (A)[b)]	(B)[c)]	Products	Yield[d)] (%)
11	 (11)	CH_3I (30)	25	5	5		75
							13
12	 (11)	CH_3I (30)	25	4	5		70
							10
13	 (11)	CH_3CH_2I (25)	25	5	5		70
							9
14	 (11)	CH_3I (30)	25	6	6		42
							22

a) Eleven mmol of $Na_2Fe(CO)_4$ were used in each run. b) Prior to addition of alkyl iodide. c) After addition of alkyl iodide. d) Based on the amount of aldehydes.



Scheme 2.

(**1**), *via* a carbonyl insertion reaction.

In these reactions, the initial adduct (**2**) (in Scheme 1) is also assumed to be an intermediate. As for the formation of benzyl acetate, the following reaction scheme is considered (Scheme 2). The adduct (**2**) is methylated at first;[13] this is followed by a carbonyl insertion reaction, the intramolecular migration of the acetyl group,[14] and protonation to give benzyl acetate. The fact that the deuteration of the reaction mixture with deuterium oxide instead of protonation gave deuterated benzyl acetate, $CH_3COOCH(D)C_6H_5$, is consistent with the scheme described above.

The effect of disodium tetracarbonylferrate (**1**) as a catalyst of the dismutation of aldehydes to the ester is assumed to be due to its high nucleophilicity. Less nucleophilic alkyl or acyl carbonylferrates(0) did not react with the aldehydes used in this reaction.

Experimental

The aldehydes were all commercial products; they were dehydrated over Drierite and distilled twice before use. The disodium tetracarbonylferrate (**1**) was prepared according to the method described in the literature.[3] The pentacarbonyliron was a commercial product and was used without further purification. The methyl iodide and ethyl iodide were also commercial products and were distilled before use. The solvent, tetrahydrofuran, was purified by distillation after being dried over lithium aluminium hydride.

Reaction of Aldehydes with ***1***. The reaction of benzaldehyde with **1** illustrates a typical procedure. Freshly distilled benzaldehyde (100 mmol) was added to a solution of 3 mmol of **1** in 25 ml of tetrahydrofuran, and the mixture was stirred at 25 °C under an argon atmosphere. After 40 h, the solvent was evaporated and the liquid thus obtained was chromatographed over alumina and then distilled to give pure benzyl benzoate(yield, 95%). The identity was established by a comparison of the spectral data(IR and NMR) and retention time of GLPC with those of an authentic sample. In the case of *p*-chlorobenzaldehyde and α-naphthaldehyde, the products were purified by recrystallization after being chromatographed.

The reaction procedure of butyraldehyde with (**1**) was as follows. To a solution of 11 mmol of (**1**) in tetrahydrofuran (40 ml), we added 0.94 g (13 mmol) of freshly distilled butyraldehyde, after which the reaction mixture was stirred at 25 °C for 3 h under an argon atmosphere. Then the mixture was poured into 50 ml of water and extracted with 50 ml of diethyl ether, after which the organic extracts were submitted to GLPC analysis. The products, 2-ethyl-2-hexenal and 2-ethylhexanal, were identified by a comparison of the retention time of the GLPC with those of authentic samples; the yields were determined using internal standards.

Successive Reaction of ***1*** *with Aldehydes and with Alkyl Iodides.* In a typical procedure, into 11 mmol of **1** in tetrahydrofuran (50 ml) we stirred 11 mmol of aldehyde in tetrahydrofuran (10 ml) at 25 °C under an argon atmosphere. A few hours later, the reaction mixture was treated with an excess of alkyl iodide and stirred for an additional 5 h. After 2 ml of water or acetic acid had then been poured into the reaction mixture, the solvent was evaporated and the residue was fractionally distilled. The esters thus obtained were identified by means of their spectral data (IR and NMR) and by a comparison of the retention time of the GLPC with those of authentic samples; the yields were determined using internal standards.

References

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8) T. Mitsudo, Y. Watanabe, T. Sasaki, H. Nakanishi, M. Yamashita, and Y. Takegami, *Tetrahedron Lett.*, **1975**, 3163.

9) The basicity of $[Fe(CO)_4]^{2-}$ is estimated to be about that of the $[OH]^-$ ion; W. Hieber and W. Hubel, *Z. Electrochem.*, **57**, 235 (1953).

10) $[FeH(CO)_4]^-$ is formed from $[Fe(CO)_4]^{2-}$ and H_2O, which is itself formed from an aldol condensate.

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12) T. A. Geissman, "Organic Reactions," Vol. 2, ed. by R. Adams, John Wiley & Sons, New York, N. Y. (1957), p. 94.

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14) The intramolecular migration of an acyl group from the cobalt to the oxygen of a carbonyl group of an aldehyde has been suggested; R. F. Heck, *J. Am. Chem. Soc.*, **87**, 4727 (1965).