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SHORT PAPER

Dimerization of aldehydes to carboxylic esters catalyzed by $K_2[Fe(CO)_4]$–crown ether system*

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$K_2[Fe(CO)_4]$ (1) with a crown ether was found to be an efficient catalyst for the dimerization of aldehydes to carboxylic esters. Several aromatic aldehydes including furfural gave the corresponding esters in good yields. This reaction also proceeded intramolecularly to give phthalide from phthalaldehyde. However, aliphatic aldehydes gave aldol-condensation products instead of the corresponding esters. In the reactions of *p*-substituted benzaldehydes with 1, the reactivity decreased with increase of the electron-releasing ability of the substituents. On the basis of these results, the reaction mechanism including the nucleophilic attack of tetracarbonylferrate dianion to the carbonyl carbon is discussed.

Keywords: Dimerization, aldehyde, carboxylic ester, tetracarbonylferrate, synthesis

INTRODUCTION

Recently, various organic reactions using organometallic compounds as a catalyst or quantitative reagent have been investigated. Metal carbonyl complexes are also utilized for this purpose in a wide variety of synthetic reactions.[1-3] In particular, iron carbonyl complexes are very useful because of their low cost and comparative lack of toxicity compared with other metal carbonyl complexes. Among them, several authors have demonstrated that alkali-metal tetracarbonylferrates ($M_2[Fe(CO)_4]$, $MH[Fe(CO)_4]$; M = Na, K) are valuable reagents for the synthesis of aldehydes, carboxylic acid derivatives, ketones and the reduction of α,β-unsaturated carbonyl compounds.[4-11]

On the other hand, benzyl benzoate 2 is used as a solvent for artificial musk, as a perfume fixative, in confectionery, and in chewing-gum flavors. For these uses, it is necessary to prepare the benzoate without any contamination by irritants and or odoriferous materials such as benzyl chlorides and/or acids.

In the course of our studies on the preparation of carboxylic esters from aldehydes, we found that reaction of 1 with 18-crown-6 catalyzes the dimerization of aromatic aldehydes. In this paper, we report the details of these ester preparations using **1** and we also discussion the reaction mechanism.

RESULTS AND DISCUSSION

By way of example, 3 mmol of **1** prepared easily by reduction of 3 mmol of $Fe(CO)_5$ by 2.1–2.5 equivalents of $KB(s\text{-}C_4H_9)_3H$,[12] reacted with 3 mmol of benzaldehyde in tetrahydrofuran (THF) under an argon atmosphere to give a trace amount of **2**. Two aldehyde groups are transformed into the corresponding alkoxyl and carboxyl functions, existing in combination as an ester.

In order to raise the yield of this reaction, several reaction conditions such as temperature and solvent were examined, but no remarkable increase of yield was observed. Then, 2 equivalents of 18-crown-6 were added to the reaction mixture in order to remove the potassium cation from the tetracarbonylferrate anion. Stirring the mixture at 60 °C for 6–7 h gave the ester in good yield (Scheme 1). This reaction proceeded by means of a catalytic amount of **1** and the crown

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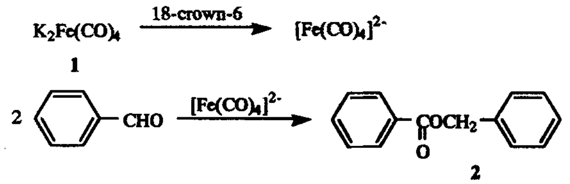
Table 1 Reaction of benzaldehyde with $K_2Fe(CO)_4$

Run	Aldehyde/$K_2Fe(CO)_4$ ratio	Reaction conditions Temp. (°C)	Time (h)	Yield (%)[a]
1	1	60	4	80.0[b]
2	5	60	7	70.5[b]
3	10	60	24	62.9[b]
4	15	60	6	71.9[b]
5	50	60	40	45.7[c]

[a] Based on the amount of aldehydes. [b] Yields were determined by GC. [c] Isolated yield.



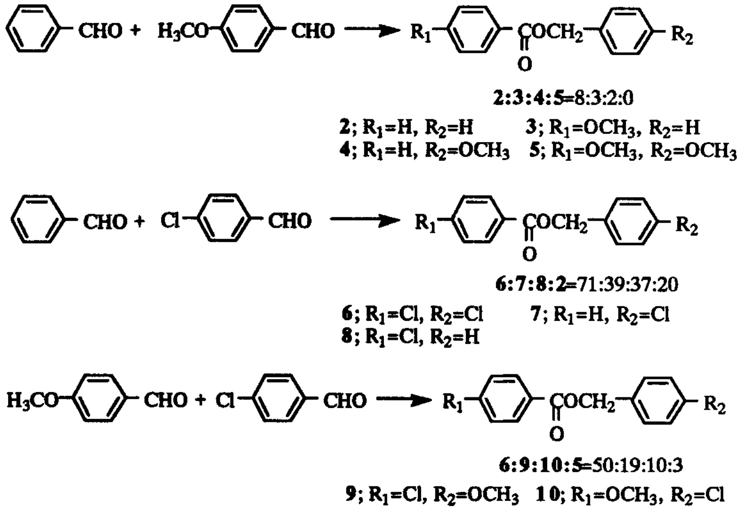
Scheme 1

ether. This effect is considered to be due to the generation of naked $[Fe(CO)_4]^{2-}$ by removal of K^+ from the tight ion-pair **1**. The results are shown in Table 1.

Under similar conditions, several aromatic aldehydes gave the corresponding esters. The results of these reactions are listed in Table 2. Benzaldehyde and *p*-chlorobenzaldehyde gave the corresponding ester **2** and **6** in 170–177% yield. In contrast, *p*-tolualdehyde and *p*-anisaldehyde, having electron-releasing substituents, produced esters **11** and **5** in lower yield, and the substantial amounts of starting materials were recovered. The by-products obtained in these reactions were small amounts of alcohols such as benzyl alcohol. Interestingly, when furfural was used, furfuryl alcohol was the main product (32.7%), showing the reduction of the carbonyl group. Moreover, this reaction also proceeded intramolecularly to give phthalide (**14**) from phthalaldehyde.

On the other hand, the treatment of aliphatic aldehydes with **1** gave completely different results. Hexanal afforded 2-butyl-2-octenal **13** and the corresponding hexyl hexanoate was not obtained. The apparent disparity is due to the basicity of $[Fe(CO)_4]^{2-}$ [the basicity of $Fe(CO)_4]^{2-}$ is estimated to be about that of the OH^- ion[13]]. In the case of aliphatic aldehydes **1** works as a base and an aldol-condensation reaction proceeds preferentially.

When terephthalaldehyde is treated with the catalyst, the corresponding polyester compounds are expected to be formed. The reaction was



2:**3**:**4**:**5**=8:3:2:0

2; R_1=H, R_2=H **3**; R_1=OCH_3, R_2=H
4; R_1=H, R_2=OCH_3 **5**; R_1=OCH_3, R_2=OCH_3

6:**7**:**8**:**2**=71:39:37:20

6; R_1=Cl, R_2=Cl **7**; R_1=H, R_2=Cl
8; R_1=Cl, R_2=H

6:**9**:**10**:**5**=50:19:10:3

9; R_1=Cl, R_2=OCH_3 **10**; R_1=OCH_3, R_2=Cl

Scheme 2

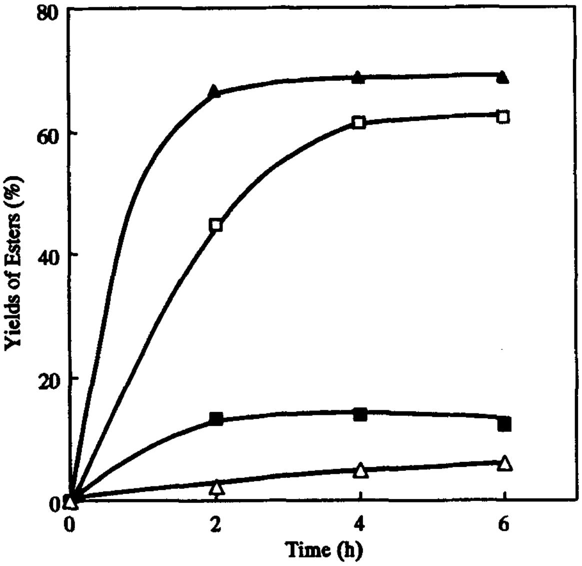


Figure 1 Yields of esters vs time plots for the reaction of **1** with aldehydes in THF, at 60 °C under argon: ▲, *p*-chlorobenzaldehyde; □, benzaldehyde; ■, *p*-tolualdehyde; △, *p*-anisaldehyde.

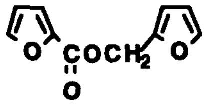
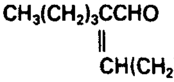
examined under several reaction conditions; it proceeded smoothly and the starting material disappeared within 6 h. Tarry material was obtained as a product in each case, although it was not analyzed.

In the reaction of *p*-substituted benzaldehydes using **1**, the remarkable influence of the substituents was observed on the reaction rates. The yields of esters vs time plots for these reactions are shown in Fig. 1. The order of their reactivities is as follows: $p\text{-ClC}_6\text{H}_4\text{CHO} > \text{C}_6\text{H}_5\text{CHO} > p\text{-CH}_3\text{C}_6\text{H}_4\text{CHO} > p\text{-CH}_3\text{OC}_6\text{H}_4\text{CHO}$. The reactivity decreased with increase of the electron-releasing property of the substituents. This suggests that the reaction is attributed to the electron density on the carbonyl carbon of the aldehydes.

Next, an equimolar mixture of two different aldehydes which have different electron density on their carbonyl carbon was treated with **1** (Scheme 2). In each case, the main product was formed by reaction of the aldehyde pair having lower electron density on the carbonyl carbon than the others. An ester derived from the aldehydes which has higher electron density on its carbonyl carbon than the other was formed in very low yield, or not formed.

On the basis of these results, the reaction mechanism is discussed (Scheme 3). First, $[\text{Fe(CO)}_4]^{2-}$ attacks the carbonyl carbon of the aldehyde nucleophilically to give an adduct **A**. The addition of the second aldehyde to **A** is followed by the loss of the $[\text{Fe(CO)}_4]^{2-}$ to give the esters. The $[\text{Fe(CO)}_4]^{2-}$ attacks the carbonyl carbon of the other aldehyde again as a catalyst. This mechanism is supported by the investigations of

Table 2 Reaction of aldehydes with $K_2Fe(CO)_4$

Run	Aldehyde (mmol)	$K_2Fe(CO)_4$ (mmol)	Conditions		Products	Yield (%)[a]
			Temp. (°C)	Time (h)		
						
1	C_6H_5CHO(5)	1	60	6	**2**; R = H	70.5[b]
2	ClC_6H_4CHO(15)	3	60	4	**6**; R = Cl	68.7[b]
3	$H_3CC_6H_4CHO$(15)	3	60	4	**11**; R = Me	14.1[b]
4	$H_3COC_6H_4CHO$(15)	3	60	45	**5**; R = OCH_3	8.0[b]
5	Furfural(9)	3	60	24	**12**: 	3.4[c]
6	*n*-Hexanal(15)	3	60	4	**13**;  $CH_3(CH_2)_3C(=CH(CH_2)_4CH_3)CHO$	50.7[c]
7	*o*-Phthalaldehyde(15)	1	60	22	**14**; Phthalide	17.1[b]
8	Terephthalaldehyde(15)	1	60	18	—[d]	—

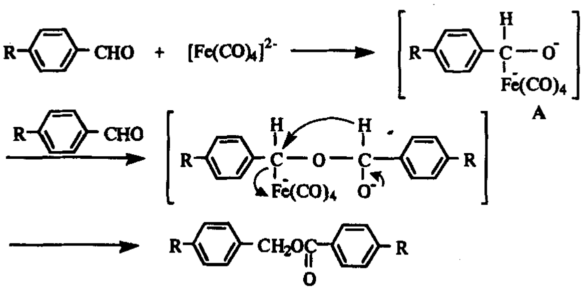
[a] Based on the amount of aldehydes. [b] Yields were determined by GC. [c] Isolated yields. [d] Tarry materials were obtained.

the effect of substituents upon the reactivity of *p*-substituted benzaldehydes. It is roughly similar to that of the well-known variations of the base-induced dismutation of aldehydes.[14]

EXPERIMENTAL

General

^{1}H NMR spectra were recorded with a Hitachi R-600 FT-NMR spectrometer operating at 60 MHz. Peak positions are reported in parts per million relative to tetramethylsilane internal standard. Spectra which were recorded without resonance decoupling have peaks reported as singlet (s), doublet (d), triplet (t), quartet (q) or multiplet (m). Infrared (IR) spectra were recorded on a Hitachi 260-10 spectrometer as KBr pellets, Nujol (for solids) or liquid film (for liquids). Mass spectra were recorded on a Hitachi M-80B or Shimazu GCMS-QP2000A instrument. Gas chromatography was performed on a Shimazu GC-14A model equipped with a capillary column (CBP 1-W12-100, 0.53 mm i.d. × 12 m) using helium as a carrier gas. All melting points were determined with Yanagimoto micro-melting-point apparatus and are uncorrected. Column chromatography was done with E. Merck silica gel 60(230–400-mesh). Analytical thin-layer chromatography (TLC) was done with E. Merck reagent silica gel 60 F-254 with a 0.25 mm thickness. Tetrahydrofuran (THF) was dried and distilled under an argon atmosphere from potassium-benzophenone just before use. The aldehydes were all commercial products; they were dehydrated over calcium sulphate and distilled before use. Potassium tri-*s*-butylhydroborate was purchased from Aldrich Chemical Co. as a 1.0 M THF solution under the trade name K-selectride. Pentacarbonyliron and 18-crown-6 were commercial products and were used without further purification.



Scheme 3

Preparation of 1

Under an argon atmosphere, $Fe(CO)_5$ (0.13 ml, 1 mmol) was added to the THF solution (2.2 ml) of 1.0 M K-selectride in a reactor. The reaction mixture was refluxed for 4 h. After cooling, the resultant colorless precipitate was washed with THF (3 × 10 ml) in the reaction flask.

Preparation of carboxylic esters

In a typical procedure, 2 mmol of 18-crown-6 and aldehydes were added to a solution of 1 mmol of **1** in 10 ml tetrahydrofuran, and the mixture was stirred at 60 °C for a certain reaction time under an argon atmosphere. Then the mixture was poured into 30 ml of water and extracted with diethyl ether. After drying over magnesium sulphate, the organic extracts were concentrated. The residual crude products were purified by column chromatography. The esters thus obtained were identified by means of their spectral data (IR, NMR and mass spectra) and by comparison of the GLC retention time with those of authentic samples; the yields were determined using internal standards. All products gave satisfactory analyses.

Benzyl benzoate (2)
IR (liquid film) 3050, 1730, 1460, 1280, 1120, 720 cm^{-1}; ^{1}H NMR($CDCl_3$) $\delta = 5.34$ (2H, s, OCH_2), 7.08–8.18 (10H, m, aromatic H); GC MS *m/z* (relative intensity) 212 (M^+, 23), 105 (100), 91 (56), 77 (40), 51 (25).

***p*-Chlorobenzyl *p*-chlorobenzoate (6)**
IR (Nujol) 1740, 1610, 1290, 1220, 790 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta = 5.30$ (2H, s, OCH_2), 7.23–8.12 (8H, m, aromatic H); GC MS *m/z* (relative intensity) 280 (M^+, 9), 139 (48), 125 (30), 86 (100), 58 (27). M.p. = 63–64 °C.

***p*-Methylbenzyl *p*-methylbenzoate (11)**
IR (Nujol) 1730, 1620, 1280, 1180, 1100, 820, 760 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta = 2.29$ (6H, s, $2 \times CH_3$), 5.20 (2H, s, OCH_2) 6.95–8.10 (8H, m, aromatic H); GC MS *m/z* (relative intensity) 240 (M^+, 30), 119 (100), 105 (48), 91 (27), 65 (14). M.p. = 35–37 °C.

***p*-Methoxybenzyl *p*-methoxybenzoate (5)**
IR (liquid film) 3000, 2860, 1720, 1620, 1520, 1270, 1180, 1120, 780 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta = 3.80$ (3H, s, OCH_3), 3.81 (3H, s, OCH_3), 5.24 (2H, s, OCH_2), 6.74–8.10 (8H, M, aromatic H).

GC MS m/z (relative intensity) 272 (M$^+$, 15), 135 (43), 121 (100), 77 (26).

Furfuryl 2-furancarboxylate (12)
IR (liquid film) 2940, 1720, 1480, 1300, 1180, 1120, 760 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta = 5.12$ (2H, s, OCH_2), 6.15–7.60 (6H, m, furan H). GC MS m/z (relative intensity) 192 (M$^+$, 15), 95 (12), 91 (100).

2-Butyl-2-octenal (13)
IR (liquid film) 2950, 1700, 1480, 1280, 800 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta = 0.70$–1.10 (6H, m, $2 \times CH_3$), 1.10–2.60 (14H, m, $7 \times CH_2$), 6.40 (1H, t, $CH{=}C$), 9.30 (1H, s, CHO). GC MS m/z (relative intensity) 182 (M$^+$, 14), 139 (21), 125 (15), 111 (36), 83 (33), 55 (100).

Phthalide (14)
IR (Nujol) 1760, 1300, 1240, 1080, 1020, 760 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta = 5.30$ (2H, s, CH_2O), 7.35–8.10 (4H, m, aromatic H). GC MS m/z (relative intensity) 134 (M$^+$, 29), 118 (20), 105 (100), 77 (38), M.p. = 72–74 °C.

Benzyl *p*-methoxybenzoate (3)
IR (liquid film) 3000, 1740, 1620, 1280, 1180, 1120, 1040, 780 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta = 3.80$ (3H, s, OCH_3), 5.30 (2H, s, OCH_2), 6.75–8.15 (9H, m, aromatic H). GC MS m/z (relative intensity) 242 (m$^+$, 10), 197 (2), 135 (100), 91 (48).

***p*-Methoxybenzyl benzoate (4)**
IR (liquid film) 3000, 1740, 1640, 1300, 1200, 1140, 740 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta = 3.80$ (3H, s, OCH_3), 5.29 (2H, s, OCH_2), 6.75–8.20 (9H, m, aromatic H). GC MS m/z (relative intensity) 242 (M$^+$, 25), 121 (100), 105 (46), 77 (52).

***p*-Chlorobenzyl benzoate (7)**
IR (liquid film) 1740, 1520, 1480, 1300, 1120, 730 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta = 5.28$ (2H, s, OCH_2) 7.15–8.18 (9H, m, aromatic H). GC MS m/z (relative intensity) 246 (M$^+$, 14), 125 (47), 105 (100), 77 (48).

Benzyl *p*-chlorobenzoate (8)
IR (liquid film) 1760, 1620, 1430, 1300, 1120, 780 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta = 5.32$ (2H, s, OCH_2), 7.10–8.12 (9H, m, aromatic H). GC MS m/z (relative intensity) 246 (M$^+$, 20), 139 (88), 111 (26), 91 (100), 75 (30).

***p*-Methoxybenzyl *p*-chlorobenzoate (9)**
IR (Nujol) 1740, 1620, 1600, 1280, 1100, 760 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta = 3.77$ (3H, s, OCH_3), 5.24 (2H, s, OCH_2), 6.72–8.10 (8H, m, aromatic H). GC MS m/z (relative intensity) 276 (M$^+$, 16), 139 (16), 121 (100). M.p. = 34–36 °C.

***p*-Chlorobenzyl *p*-Methoxybenzoate (10)**
IR (KBr) 1700, 1600, 1500, 1260, 1180, 800 cm^{-1}; ^{1}H NMR ($CDCl_3$) $\delta = 3.82$ (3H, s, OCH_3), 5.28 (2H, s, OCH_2), 6.70–8.20 (8H, m, aromatic H). GC MS m/z (relative intensity) 276 (M$^+$, 8), 231 (3), 135 (100), 125 (39). M.p. = 78–80 °C.

CONCLUSIONS

1 and the 18-crown-6 system was found to be an efficient catalyst for the conversion of aromatic aldehydes to carboxylic esters. This reaction proceeded not only intermolecularly but also intramolecularly to give the esters and lactones in good yields and, as **1** was easily prepared from $Fe(CO)_5$ and $K(s\text{-}C_4H_9)_3BH$, it may become a good synthetic method for carbooxylic esters from aldehydes.

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