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Synthesis of Carboxylic Esters from Aldehydes using Metal Carbonyl Anions, Part 2. Dimerization of Aldehydes to Carboxylic Esters Catalyzed by Disodium Pentacarbonylchromate, $Na_2[Cr(CO)_5]$*

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$Na_2[Cr(CO)_5]$ (1) 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. Compared with $M_2[Fe(CO)_4]$ (M = Na, K), 1 was found to be a more efficient catalyst for this reaction. 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 the increase of the electron-releasing ability of the substituents. However, even *p*-anisaldehyde, which hardly reacted with $M_2[Fe(CO)_4]$, reacted with 1 to give the ester in moderate yield. The reaction mechanism, including the nucleophilic attack of the pentacarbonylchromate dianion on the carbonyl carbon, is discussed.

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

INTRODUCTION

Recently, various organic reactions using organometallic compounds as catalysts or as quantitative reagents have been investigated. Metal carbonyl complexes are also utilized for this purpose in a wide variety of synthetic reactions.[1–3] Previously, we have reported that disodium and dipotassium tetracarbonylferrate $M_2[Fe(CO)_4]$ (M = Na, K) have been shown to be good catalysts for disproportional dimerization of two molecules of aldehyde to carboxylic ester,[4] for example two molecules of benzaldehyde to benzyl benzoate which is used as a solvent for artificial musk, as a perfume fixative, in confectionery, and in chewing gum flavors. In the course of our study by preparing carboxylic esters from aldehydes, in order to avoid contamination by irritant and noxious materials such as benzyl chlorides and/or acids, we found that $Na_2[Cr(CO)_5]$ (1) catalyzes this dimerization of aldehydes more effectively. In this paper, we report the details of these ester preparations using 1 and we discuss the reaction mechanism.

RESULTS AND DISCUSSION

For example, 1, prepared *in situ* by reduction of 3 mmol of $Cr(CO)_6$ by two equivalents of sodium-naphthalene in tetrahydrofuran (THF), reacted with 45 mmol of benzaldehyde at 60 °C under an argon atmosphere to give 19.1 mmol (84.9% yield based on benzaldehyde, catalytically 1273% based on 1) of benzyl benzoate, 2 (Scheme 1). Two aldehyde groups are transformed into the corresponding alkoxyl and carboxyl functions, existing in combination as an ester. The results are shown in Table 1.

As shown in Table 1, when 50 molar equiva-

2

Scheme 1

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Table 1 Reaction of benzaldehyde with $Na_2Cr(CO)_5$

Run	Aldehyde/$Na_2Cr(CO)_5$ ratio	Time (h)	Yield (%)[a, b]
1	1	3	11
2	10	2	437
3	15	2.5	637
4	30	18	1150
5	40	21	1900
6	50	18	2100

[a] Based on the amount of benzaldehyde, i.e. sometimes catalytic. [b] Determined by GC.

lents of benzaldehyde was used, a catalytic 2100% yield of **2** based on **1** was obtained. In the reaction using $K_2Fe(CO)_4$, **3**, with 18-crown-6 as a catalyst,[4] the yield was 1143% based on **3**, showing that **1** is a more effective catalyst than **3** even without the addition of crown ether.

The effect of reaction temperature was as follows: the reaction proceeded at room temperature, but as shown in Fig. 1, elevation of the temperature from room temperature to 60 °C increased the yield of the product. Therefore the following reactions were conducted at 60 °C.

Under similar conditions, several aromatic aldehydes gave the corresponding esters. The results of these reactions and time plots are listed in Table 2 and Fig. 2. Besides benzaldehyde, *p*-chlorobenzaldehyde (which has an electron-withdrawing substituent on the benzene ring) gave the corresponding ester, *p*-chlorobenzyl *p*-chlorobenzoate, in highest yield among those investigated. Even *p*-tolualdehyde and *p*-anisaldehyde, which have electron-releasing substituents and have poor reactivity toward tetracarbonylferrate anion **3**, reacted with the chromate anion **1** rather smoothly, to give (respectively) esters *p*-methylbenzyl *p*-methylbenzoate and *p*-methoxybenzyl *p*-methoxybenzoate in moderate yields, although substantial amounts of starting materials were recovered too. Furfural also gave the corresponding ester in moderate yield (144% on **1**), while furfuryl alcohol was the main product (32.7%) when **3** was used as a catalyst. The by-products obtained in these reactions included small amounts of alcohols such as benzyl alcohol. Moreover, this reaction also proceeded intramolecularly to give phthalide in 983% yield from phthalaldehyde.

When terephthalaldehyde was treated with the catalyst, the corresponding polyester compounds were expected to be formed. Therefore, the reaction was examined under several reaction conditions. However, only *p*-hydroxymethylbenzaldehyde was obtained in 39% yield and the starting material was recovered.

The reaction mechanism was assumed to be as follows (Scheme 2). Reduction of $Cr(CO)_6$ by sodium-naphthalene gives a mixture of **1** with contaminated $[Cr_2(CO)_{10}]^{2-}$ (**4**). As **4** has been reported to be prepared by the reduction of $Cr(CO)_6$ by sodium-amalgam in THF,[5] we prepared **4** and the resulting solution was submitted to reaction with benzaldehyde. However, no corresponding ester was obtained, showing the inactivity of **4** to this reaction. Therefore, the active catalyst is considered to be **1**.

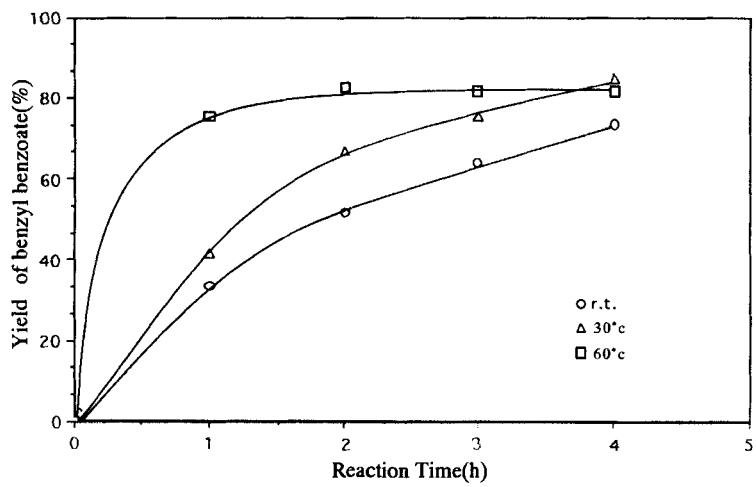
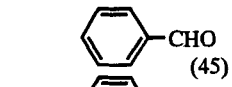
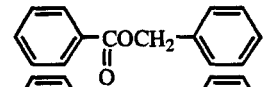
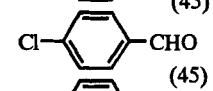
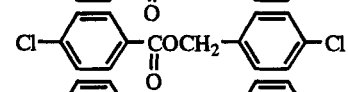
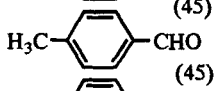
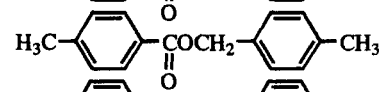
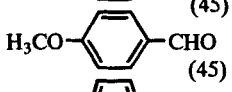
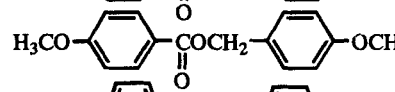
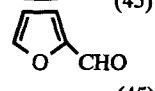
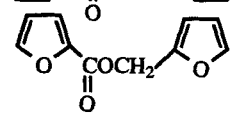
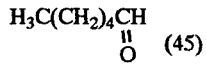
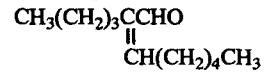
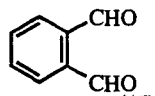
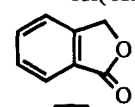
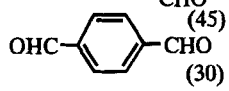
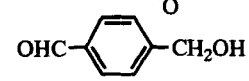


Figure 1 Yields of benzyl benzoate vs time plots for the reaction of $Na_2Cr(CO)_5$ with benzaldehyde (in THF, under argon).

Table 2 Reactions of aldehydes with $Na_2Cr(CO)_5$

Run	Aldehyde (mmol)	Conditions: Temp. (°C)	Time (h)	Product	Yield (%)[a]
1	 (45)	60	2.5		84.9[b] (1274)
2	 (45)	60	4		94.2[b] (1413)
3	 (45)	60	7		48.4[b] (726)
4	 (45)	60	6		49.8[b] (747)
5	 (45)	60	20		9.6[c] (144)
6	 (45)	60	18		11.2[c] (168)
7	 (45)	60	18		65.5[c] (983)
8	 (30)	60	43		3.9[c] (39)

[a] Based on the amount of aldehyde. Yields in parentheses are based on $Na_2Cr(CO)_5$—catalytic. [b] Yields were determined by GC. [c] Isolated yields.

The chromate **1** attacks the carbonyl carbon of the aldehyde nucleophilically to give an adduct **5**. The addition of the second aldehyde to **5** is followed by loss of $[Cr(CO)_5]^{2-}$ to give the esters. The $[Cr(CO)_5]^{2-}$ attacks the carbonyl carbon of the other aldehyde again as a catalyst. This mechanism is supported by investigation of the effects of substituents upon the reactivity of *p*-

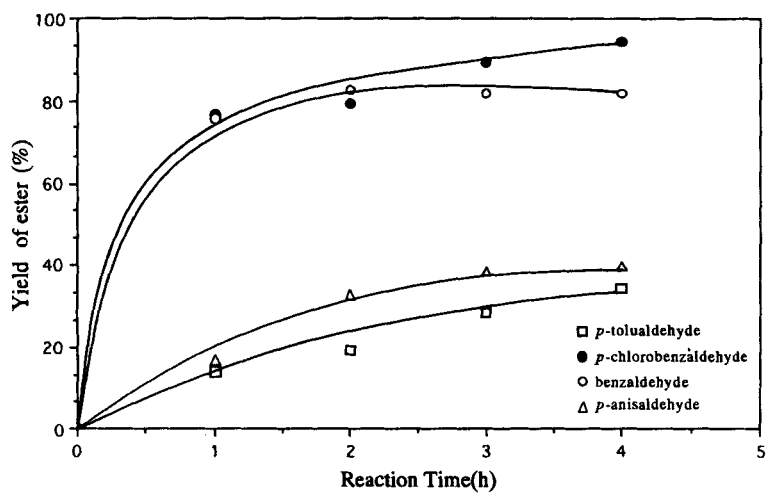
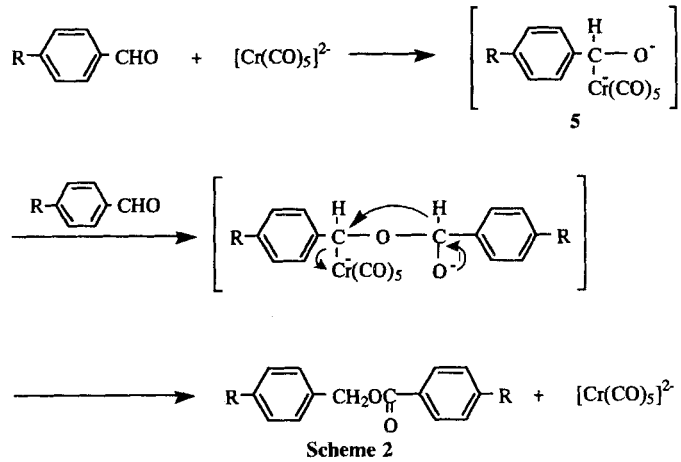


Figure 2 Yields of ester versus time plots for the reaction of $Na_2Cr(CO)_5$ with aldehydes (in THF, at 60 °C under argon).



Scheme 2

substituted benzaldehydes. It is roughly similar to that of the well-known variations of the base-induced dismutation of aldehydes.[6]

On the other hand, treatment of aliphatic aldehydes with **1** gave completely different results. For example, hexanal afforded 2-butyl-2-octenal and the corresponding hexyl hexanoate was not obtained. This apparent disparity is due to the basicity of $[Cr(CO)_5]^{2-}$ and/or $[Cr_2(CO)_{10}]^{2}$.[7,8] In the case of aliphatic aldehydes, the dianions work as a base and the aldol condenstion reaction proceeds preferentially.

EXPERIMENTAL

General

Proton nuclear magnetic resonance (^{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 with off-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 carrier gas. All melting points were determined with a Yanagimoto micro melting point apparatus and are uncorrected. Column chromatography was done with E. Merck reagent silica gel 60 (230–400 mesh). Analytical thin-layer chromatography (TLC) was performed with E Merck reagent silica gel 60 F-254, 0.25 mm thick. 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. Hexacarbonylchromium was a commercial product and was used without further purification.

Preparation of 1

Under an argon atmosphere, $Cr(CO)_6$ (0.66 g, 3 mmol) was added to the THF solution (10 cm^3) of sodium-naphthalene (6 mmol) which was prepared by the reaction of naphthalene (0.77 g, 6 mmol) and sodium metal (0.14 g, 6 mmol) in THF (10 cm^3). The reaction mixture was stirred for 1 h at room temperature and the solution was used in the following reaction.

Preparation of carboxylic esters

In a typical procedure, 45 mmol of aldehyde was added to a solution of 3 mmol of **1** in 10 cm^3 of THF, and the mixture was stirred at 60 °C for 2.5 h under an argon atmosphere. Then the mixture was poured into 30 cm^3 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 deta (IR, NMR and MS) and by comparison of the retention time of the GLC with that of

an authentic sample; 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}; ^1H 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**
IR (Nujol): 1740, 1610, 1290, 1220, 790 cm^{-1}; ^1H 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**
IR (Nujol): 1730, 1620, 1280, 1180, 1100, 820, 760 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 2.29$ (6H, s, $CH_3 \times 2$), 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**
IR (liquid film): 3000, 2860, 1720, 1620, 1520, 1270, 1180, 1120, 780 cm^{-1}; ^1H 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
IR (liquid film): 2940, 1720, 1480, 1300, 1180, 1120, 760 cm^{-1}; ^1H NMR($COCl_3$): $\delta = 5.12$ (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
IR (liquid film): 2950, 1700, 1480, 1280, 800 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 0.70$–1.10 (6H, m, $CH_3 \times 2$), 1.10–2.60 (14h, m, $CH_2 \times 7$), 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
IR (Nujol): 1760, 1300, 1240, 1080, 1020, 760 cm^{-1}; ^1H 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.

CONCLUSIONS

Compound **1** 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. As **1** was easily prepared from $Cr(CO)_6$ and sodium-naphthalene, this reaction may become a good synthetic method for carboxylic esters from aldehydes.

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