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REDUCTIVE COUPLING OF AROMATIC ALDEHYDES BY OCTACARBONYL DIFERRATE

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The reaction of aromatic aldehydes with $Fe(CO)_5$ or $Fe_3(CO)_{12}$ in pyridine gives the corresponding 1,2-diaryl-1,2-ethanediols as major products in good yields. A reactive species of this reaction is octacarbonyl diferrate $[Fe_2(CO)_8]^{2-}$.

Recently, mononuclear carbonyl ferrates such as $[Fe(CO)_4]^{2-}$ and $[HFe(CO)_4]^-$ have been proved to be useful reagents in organic synthesis.[1,2] However, the synthetic utility of polynuclear carbonyl ferrates have little been developed.[3] Previously, we reported that a polynuclear ferrate, which was prepared from $Fe_3(CO)_{12}$ and pyridine N-oxide, effectively promotes the reductive coupling of benzylic and allylic halides.[4] We now report that a dinuclear carbonyl ferrate, which is prepared by treating iron carbonyls with pyridine,[5] induces the reductive coupling of aromatic aldehydes to give the corresponding 1,2-diaryl-1,2-ethanediols.[6]

A solution of $Fe_3(CO)_{12}$ (2.0 mmol) and benzaldehyde [1a] (20 mmol) in pyridine (10 ml) was heated at 80°C under N_2 atmosphere for 1.5 h. Water (10 mmol) was added, and the mixture was heated again at 80°C for 18.5 h and then treated with 6 M hydrochloric acid (10 ml) at room temperature for 30 min.[7] The resulting mixture was extracted with benzene (10 ml). The extract was washed with water and dried over Na_2SO_4. Upon adding petroleum ether to the extract, 1,2-diphenyl-1,2-ethanediol [2a] (5.1 mmol) precipitated as crystals which were separated by filtration. The filtrate was concentrated and chromatographed on silica gel. Elution with benzene gave recovered [1a] (7.1 mmol). Subsequent elution with benzene-ether afforded [2a] (0.72 mmol) and benzyl alcohol [3a] (0.78 mmol). The total yield of [2a] based on the reacted [1a] was 91%, and that based on $Fe_3(CO)_{12}$ used was 294%.

$$\underset{[1a\text{-}f]}{RC_6H_4CHO} \xrightarrow[\text{2) } H_2O \text{ and } H_3O^+]{\text{1) } Fe(CO)_5,\ Fe_3(CO)_{12}/\text{Pyridine}} \underset{[2a\text{-}f]}{RC_6H_4CH(OH)CH(OH)C_6H_4R} + \underset{[3a\text{-}f]}{RC_6H_4CH_2OH}$$

a: R=H, b: R=o-CH_3, c: R=m-CH_3, d: R=p-CH_3, e: R=p-Cl, f: R=p-CH_3O

Table 1. Reaction of Aromatic Aldehydes and Ketones with Iron Carbonyls in Pyridine[a)]

Run	Aromatic Substrate	Iron Carbonyl	Time (h)	Products, Yield %[b)] [2]	[3]
1	[1a]	$Fe(CO)_5$	14	88 (88)	11 (5.5)
2	[1a]	$Fe_3(CO)_{12}$	20[c)]	294 (91)	39 (6.0)
3	[1b]	$Fe(CO)_5$	20[c)]	82 (81)	22 (11)
4	[1b]	$Fe_3(CO)_{12}$	20[c)]	274 (80)	89 (14)
5	[1c]	$Fe(CO)_5$	20[c)]	76 (76)	25 (13)
6	[1c]	$Fe_3(CO)_{12}$	20[c)]	233 (72)	90 (13)
7	[1d]	$Fe(CO)_5$	20[c)]	85 (79)	34 (16)
8	[1d]	$Fe_3(CO)_{12}$	20[c)]	252 (78)	122 (19)
9	[1e]	$Fe(CO)_5$	20	77 (74)	26 (13)
10	[1e]	$Fe_3(CO)_{12}$	20	262 (84)	63 (10)
11	[1f]	$Fe(CO)_5$	20[c)]	31 (95)	—
12	[1f]	$Fe_3(CO)_{12}$	20[c)]	134 (96)	—
13	$C_6H_5COCH_3$	$Fe_3(CO)_{12}$	20	no reaction	
14	$C_6H_5COC_6H_5$	$Fe_3(CO)_{12}$	20	no reaction	

a) A solution of $Fe(CO)_5$ (6.0 mmol) or $Fe_3(CO)_{12}$ (2.0 mmol) and a substrate (20 mmol) in pyridine (10 ml) was heated at 80°C for 20 h except Run 1. b) The yields based on the iron carbonyl used, and those in parentheses based on aldehydes reacted. c) A small amount of water (10 mmol) was added after heating the solution at 80°C for the following periods of time; 1.5 h in Runs 2 and 8, and 5 h in the other Runs.

Similar treatment of substituted benzaldehydes [1b-f] with $Fe_3(CO)_{12}$ in pyridine gave the corresponding 1,2-diaryl-1,2-ethanediols [2b-f] as major products and the corresponding benzyl alcohols [3b-f] as minor products. The reaction of [1a-f] with $Fe(CO)_5$ in pyridine also yielded the same products, [2a-f] and [3a-f], but with lower efficiency. However, no reaction occurred when acetophenone and benzophenone were treated with $Fe_3(CO)_{12}$ in pyridine under similar conditions. The results are summarized in Table 1.

In order to elucidate a mechanistic feature of these reactions, the reactions of [1a] with $Fe(CO)_5$ and $Fe_3(CO)_{12}$ in pyridine were conducted under the similar conditions as above. Then, amounts of [2a] produced were determined at appropriate time intervals by VPC analysis of the reaction mixture. The results are shown in Fig. 1. The induction period in the reaction using $Fe_3(CO)_{12}$ was much shorter than that in the reaction using $Fe(CO)_5$. However, amounts of [2a] produced per one Fe atom of each iron carbonyl were approximately equal for both $Fe_3(CO)_{12}$ and $Fe(CO)_5$; that is, one molar amount of [2a] was produced from one atom equiv of Fe in both cases.

Evolution of CO was observed even when pyridine solutions of $Fe(CO)_5$ and

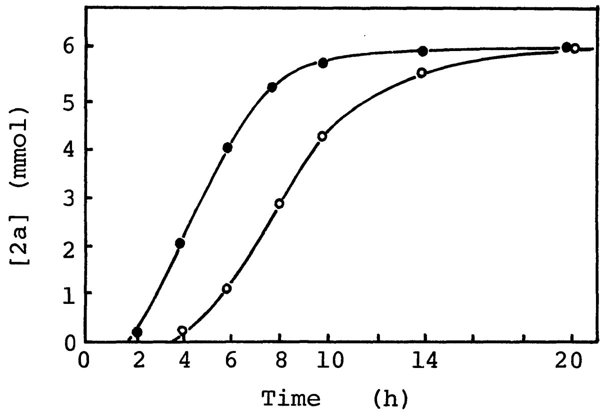

Fig.1 Rates of formation of [2a].
A mixture of [1a] (20 mmol) and $Fe(CO)_5$ (6 mmol) or $Fe_3(CO)_{12}$ (2 mmol) in pyridine (10 ml) was heated at 80°C for 5 h in the case of $Fe(CO)_5$ and for 1.5 h in the case of $Fe_3(CO)_{12}$, and water (10 mmol) was added. Then, the mixture was heated at 80°C. ○ : $Fe(CO)_5$, ● : $Fe_3(CO)_{12}$.

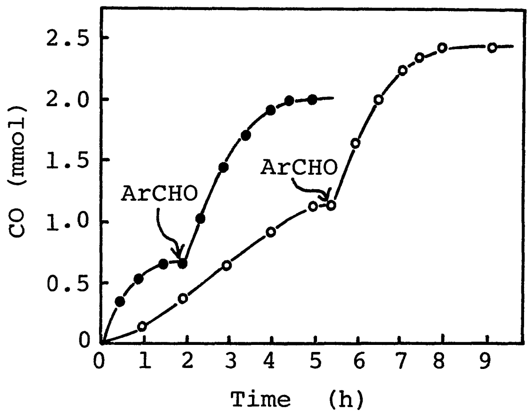

Fig.2 Amounts of CO on the reaction time.
$Fe(CO)_5$=0.48 mmol, $Fe_3(CO)_{12}$=0.16 mmol, Pyridine=5 ml, [1a]=10 mmol.
○ : $Fe(CO)_5$, ● : $Fe_3(CO)_{12}$.

$Fe_3(CO)_{12}$ were heated at 80°C in the absence of [1a]. After evolution of CO ceased, further evolution of CO commenced as soon as [1a] was added to the above mixtures. Amounts of CO evolved during these reactions are shown in Fig.2. In the case of $Fe(CO)_5$, approximately 7/3 molar equiv of CO evolved from one molar amount of $Fe(CO)_5$. While, in the reaction of $Fe_3(CO)_{12}$, approximately 4 molar equiv of CO evolved from one molar amount of $Fe_3(CO)_{12}$. On the other hand, amounts of CO evolved after the addition of [1a] and its evolution rates were approximately equal for $Fe(CO)_5$ and $Fe_3(CO)_{12}$.

To isolate a key intermediate of the reaction, $Fe_3(CO)_{12}$ (2.0 mmol) was heated in pyridine (10 ml) at 80°C for 1 h, and then the mixture was treated with a CH_2Cl_2 solution of bis(triphenylphosphine)iminium chloride $[(Ph_3P)_2N]Cl$ (2.44 mmol). Work-up of this mixture gave the dinuclear ferrate complex $[(Ph_3P)_2N]_2[Fe_2(CO)_8]$.[8)]

From the above results, we presumed the reaction pathways of Scheme 1 for the reactions reported in this paper. The reactions of $Fe(CO)_5$ and $Fe_3(CO)_{12}$ with pyridine give the octacarbonyl diferrate [4]. The rate of formation of [4]

$$\left.\begin{array}{l} 3\,Fe(CO)_5 \;+\; n\,C_5H_5N \xrightarrow{\;-7CO\;} \\[1ex] Fe_3(CO)_{12} \;+\; n\,C_5H_5N \xrightarrow{\;-4CO\;} \end{array}\right] \longrightarrow \underset{[4]}{[Fe(C_5H_5N)_n][Fe_2(CO)_8]}$$

$$[4] \;+\; 6\,ArCHO \xrightarrow{H_2O,\;H_3O^+} 3\,ArCH(OH)CH(OH)Ar \;+\; 8\,CO \;+\; 3\,Fe^{2+} \;+\; n\,C_5H_5N$$

Scheme 1

is faster for $Fe_3(CO)_{12}$ than for $Fe(CO)_5$ (see Fig.2). Complex [4] induces the reductive coupling of aromatic aldehydes with concomitant oxidation of [4] to Fe(II) ions and evolution of CO. In the presence of water, [4] induces the reduction of aldehydes, giving benzyl alcohols as by-products. An active species of this reaction may be a hydrido complex of [4].9)

On the contrary, disodium tetracarbonyl ferrate $Na_2Fe(CO)_4$, a mononuclear ferrate, was shown to react with aromatic aldehydes to give the corresponding benzyl benzoates.10) The reactivity of the dinuclear ferrate is apparently different from that of the mononuclear ferrate.

References and Notes

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6) Recently, it has been demonstrated that the reductive coupling of aldehydes can also be effected by low-valent titanium reagents: E. J. Corey, R. L. Danheiser, and S. Chandrasekaran, J. Org. Chem., 41, 260 (1976), and references cited therein.

7) When [1a] was treated with $Fe_3(CO)_{12}$ in pyridine at 80°C for a longer period of time (20 h) in the absence of water, benzoin and [2a] were obtained in a 3:1 ratio in the total yield of 270% based on $Fe_3(CO)_{12}$ used, together with a small amount of [3a].

8) The following analytical and spectral data were obtained for $[(Ph_3P)_2N]_2[Fe_2(CO)_8]$. Found: C, 67.78; H, 4.27; Fe, 7,99; N, 1.83%. Calcd. for $C_{80}H_{60}Fe_2N_2O_8P_4$: C, 68.00; H, 4.28; Fe, 7.91; N, 1.98%. IR (KBr), 1930 cm^{-1}, 1910 cm^{-1}, 1870 cm^{-1}.

9) Aromatic aldehydes are reduced by hydrido ferrates to give the corresponding alcohols: H. W. Sternberg, R. Markby, and I. Wender, J. Am. Chem. Soc., 78, 5704 (1956); H. W. Sternberg, R. Markby, and I. Wender, ibid., 79, 6116 (1957).

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