

to a doublet ( $J = 6.1$  Hz). In addition, a signal at 2.57 ppm was observed for the syn diastereomer ( $J = 3.9$  Hz). Anal. Calcd for  $C_{12}H_{16}O_3$ : C, 69.21; H, 7.74. Found: C, 69.43; H, 7.82.

**Methyl threo-3-hydroxy-2-methyl-4-cyclohexylbutanoate (4b):**<sup>21</sup>  $^1H$  NMR (250 MHz)  $\delta$  3.70 (s, 3 H) 3.44 (pseudotriplet,  $J = 6$  Hz, 1 H), 2.72 (pseudoquintet,  $J = 7$  Hz, 1 H), 1.9-1.5 (m, 6 H), 1.5-1.0 (d at 1.21 ppm ( $J = 7.1$  Hz) superimposed on multiplet, total 8 H). Irradiation of the doublet at 1.21 ppm caused collapse of the signal at 2.72 ppm to a doublet ( $J = 5.9$  Hz).

**Methyl threo-3-hydroxy-2,4,4-trimethylpentanoate (4c):**<sup>22</sup>  $^1H$  NMR (250 MHz)  $\delta$  3.70 (s, 3 H), 3.24 (d,  $J = 2.0$  Hz, 1 H), 2.77 (qd,  $J = 7.2, 2.0$  Hz, 1 H), 1.35 (d,  $J = 7.2$  Hz, 3 H), 0.89 (s, 9 H).

**Methyl threo-3-hydroxy-2-methyl-3-phenylpropanoate (4d):**<sup>23</sup>  $^1H$  NMR (250 MHz)  $\delta$  7.36-7.26 (m, 5 H), 4.77 (d,  $J = 8.6$  Hz, 1 H), 3.74 (s, 3 H), 2.84 (pseudoquintet, 1 H), 1.02 (d,  $J = 7.1$  Hz, 3 H).

**(±)-Methyl [2R,3R,4S]-3-hydroxy-2-methyl-4-phenylpentanoate (4f):**<sup>24</sup>  $^1H$  NMR (250 MHz) 7.39-7.03 (m, 5 H), 3.65-3.53 (s at 3.60 ppm superimposed on m, total 4 H), 2.78 (pseudoquintet,  $J = 7.1$  Hz, 1 H), 2.38 (qd,  $J = 7.2, 4.6$  Hz, 1 H), 1.24 (d,  $J = 7.0$  Hz, 3 H), 1.12 (d,  $J = 7.2$  Hz, 3 H). Irradiation at 1.24 ppm collapsed the signal at 2.78 ppm (d,  $J = 7.6$  Hz)

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whereas irradiation at 1.12 ppm collapsed the signal at 2.38 ppm (d,  $J = 4.6$  Hz).

**(±)-Methyl [2S,3R,4R]-3-hydroxy-2-methyl-4-phenylpentanoate (4f):**<sup>24</sup> mp 57-59 °C (lit.<sup>24</sup> mp 59-60 °C);  $^1H$  NMR (250 MHz)  $\delta$  7.20-7.10 (m, 5 H), 3.72 (pseudo t,  $J = 5.5$  Hz, 1 H), 3.54 (s, 3 H), 2.81 (pseudoquintet,  $J = 7$  Hz, 1 H), 2.45 (pseudoquintet,  $J = 7$  Hz, 1 H), 1.26 (d,  $J = 7.2$  Hz, 3 H), 1.17 (d,  $J = 7.2$  Hz, 3 H). Irradiation at 1.26 ppm collapsed the signal at 2.81 ppm (d,  $J = 5.3$  Hz) whereas irradiation at 1.17 ppm collapsed the signal at 2.45 ppm (d,  $J = 5.9$  Hz).

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**Registry No.** 1 (R = H), 1271-19-8; 1 (R = Me), 1282-40-2; 1 (R = *i*-Pr), 12130-65-3; 2 (R = H), 12087-70-6; 2 (R = Me), 116148-77-7; 2 (R = *i*-Pr), 116148-78-8; *anti*-3a, 106651-02-9; *syn*-3a, 116129-24-9; *anti*-3b, 106650-99-1; *syn*-3b, 106651-03-0; *anti*-3c, 81437-87-8; *syn*-3c, 81437-88-9; *anti*-3d, 63553-62-8; *syn*-3d, 63553-63-9; *anti*-3e, 116129-25-0; *syn*-3e, 116129-26-1; 3f (Cram product), 68040-43-7; 3f (*syn*-Cram product), 116183-26-7; 3f (Cram Ac derivative), 116129-27-2; 3f (*syn*-Cram Ac derivative), 116183-28-9; 3f', 68070-07-5; 3f' (Ac derivative), 116183-27-8; *anti*-4a, 116129-28-3; *syn*-4a, 116129-29-4; *anti*-4b, 116183-29-0; *anti*-4c, 116183-30-3; *anti*-4d, 116129-30-7; 4f, 40954-97-0; 4f', 40954-96-9; PhCH<sub>2</sub>CHO, 122-78-1; *c*-C<sub>6</sub>H<sub>11</sub>CHO, 2043-61-0; *t*-BuCHO, 630-19-3; PhCHO, 100-52-7; 1,3-butadiene, 106-99-0; mesitylaldehyde, 487-68-3; (±)- $\alpha$ -methylphenylacetaldehyde, 34713-70-7.

## Scope and Mechanism of the Phase-Transfer Carbonylation of Organic Halides Catalyzed by Pentacarbonyliron To Give Ketones and Carboxylic Acids

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Various substituted benzyl halides are readily converted into 1,3-diaryl-2-propanones, RCOR, or arylacetic acids, RCO<sub>2</sub>H (R = ArCH<sub>2</sub>), under CO pressure on reaction with a catalytic amount of pentacarbonyliron in a liquid-liquid phase transfer (PT) system (CH<sub>2</sub>Cl<sub>2</sub> (or C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>)/H<sub>2</sub>O, NaOH, (Bu<sub>4</sub>N<sup>+</sup>)<sub>2</sub>SO<sub>4</sub><sup>2-</sup>). These reactions involve the in situ generation of the acyltetracarbonyliron anion, RCOFe(CO)<sub>4</sub><sup>-</sup>, which is maintained in the organic phase as the tetrabutylammonium ion pair. Further reaction of benzyl halides with this anion starts the catalytic conversion to give either ketones, RCOR, or acids, RCO<sub>2</sub>H. With less reactive halides such as alkyl bromides (for instance, RX = *n*-C<sub>4</sub>H<sub>9</sub>Br), the reaction stops after the stoichiometric conversion of Fe(CO)<sub>5</sub> into the acyl anion, RCOFe(CO)<sub>4</sub><sup>-</sup>. A detailed examination of the reaction was made by using benzyl bromide (RX = C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>Br) as the organic substrate. Selectivity toward formation of a ketone, RCOR, or an acid, RCO<sub>2</sub>H (R = C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>), as the dominant product depends on the aqueous concentration of the hydroxide anion, the stirring speed, the temperature, and the CO pressure. From these results and a kinetic study, it is inferred that two catalytic cycles compete in the PT system, both involving the acyl anion RCOFe(CO)<sub>4</sub><sup>-</sup> and the neutral complex RCOFe(CO)<sub>4</sub>R. Reductive elimination from the latter unstable complex gives rise to the ketone, RCOR, whereas PT base-catalyzed cleavage with hydroxide generates the acid, RCO<sub>2</sub>H, and the acyl anion, RCOFe(CO)<sub>4</sub><sup>-</sup>. Two catalytic cycles are proposed for these reactions.

The use of metal carbonyl derivatives in organic synthesis or catalysis under homogeneous conditions is well established.<sup>1</sup> Recent reviews have shown the great interest of the application of the phase transfer (PT) principle<sup>2</sup> for many of these reactions, particularly in the area of car-

bonylation; the advantages are (i) mild and simple reaction conditions, (ii) unexpected reactivity due to the unusual

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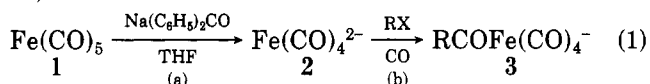
Table I. PT Carbonylation of Benzyl Bromide with Fe(CO)<sub>5</sub>: Effect of Some Parameters on the Product Ratios<sup>a</sup>

run	liquid-liquid system	Fe(CO) <sub>5</sub> /RX ratio	base (mL <sup>-1</sup> )	atmosphere (P, atm)	T, °C	stirring speed, rpm	reactn time, h	products <sup>b</sup>				
								RCO <sub>2</sub> H (7)	RCO <sub>2</sub> R (10)	RCOR (6)	RR (8)	RH (9)
1	H <sub>2</sub> O/CH <sub>2</sub> Cl <sub>2</sub>	1/10	NaOH (1)	CO (60)	20	1200	4.5	81	8	6	3	0
2	H <sub>2</sub> O/CH <sub>2</sub> Cl <sub>2</sub>	1/50	NaOH (1)	CO (60)	25	1200	27	66	8	11	4	0
3	CH <sub>3</sub> OH	1/10	NaOH (1)	CO (60)	50	1200	8	7 <sup>c</sup>				22
4	H <sub>2</sub> O/CH <sub>2</sub> Cl <sub>2</sub> <sup>d</sup>	1/10	NaOH (1)	CO (1)	20	1200	3.5	73	6	12	6	0
5	H <sub>2</sub> O/CH <sub>2</sub> Cl <sub>2</sub>	1/10	NaOH (1)	CO (1)	30	1200	4.5	50	16	35	5	0
6	H <sub>2</sub> O/CH <sub>2</sub> Cl <sub>2</sub>	1/5	NaOH (1)	CO (1)	30	1200	15	39	7	47	6	7
7	H <sub>2</sub> O/CH <sub>2</sub> Cl <sub>2</sub>	1/10	NaOH (1)	CO (1)	20	1000	4	57	7	30	4	3
8	H <sub>2</sub> O/CH <sub>2</sub> Cl <sub>2</sub>	1/10	NaOH (1)	CO (1)	20	800	6	28	18	41	5	3
9	H <sub>2</sub> O/PhMe	1/10	NaOH (1)	CO (1)	20	1200	16	75	3	14	6	2
10	H <sub>2</sub> O/PhMe	1/10	NaOH (1)	CO (1)	30	1200	17	62	2	27	12	0
11	H <sub>2</sub> O/PhMe	1/10	NaOH (2)	CO (1)	30	1200	17	62		29	17	0
12	H <sub>2</sub> O/CH <sub>2</sub> Cl <sub>2</sub>	1/10 <sup>e</sup>	NaOH (1)	CO (1)	20	1200	5	70	11	19	3	0
13	H <sub>2</sub> O/CH <sub>2</sub> Cl <sub>2</sub>	1/2	Ca(OH) <sub>2</sub> (satd)	N <sub>2</sub> (1)	20	1200	3	22	0	78	0	0
14	H <sub>2</sub> O/CH <sub>2</sub> Cl <sub>2</sub>	1/2	Ca(OH) <sub>2</sub> (satd)	CO (50)	20	1200	1.5	70	6	7	5	0
15	H <sub>2</sub> O/PhM <sub>2</sub>	1/5	Ca(OH) <sub>2</sub> (satd)	CO (1)	35	1200	6	38	1	41	2	0

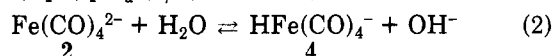
<sup>a</sup> General reaction conditions: two-phase system, 10 mL/10 mL; 2.5 mmol of C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>Br; 0.5 mmol of Bu<sub>4</sub>N<sup>+</sup>HSO<sub>4</sub><sup>-</sup>; thermostated glass cell (apparatus A) for experiments at atmospheric pressure; stainless-steel autoclave (apparatus B) for others. <sup>b</sup> Yields vs introduced benzyl bromide. Material balance within 95–108% of introduced benzyl bromide. <sup>c</sup> Main product: C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>OCH<sub>3</sub> resulting from the Williamson reaction. <sup>d</sup> The amount of CO<sub>2</sub> produced (and found as the carbonate anion in the aqueous phase) was determined for run 4:104% vs introduced Fe(CO)<sub>5</sub>. <sup>e</sup> 0.25 mmol of Bu<sub>4</sub>N<sup>+</sup>[(CO)<sub>4</sub>FeCOCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]<sup>-</sup> introduced in the place of Fe(CO)<sub>5</sub>.

features of PT systems, and (iii) in some cases, good separation of the catalyst from the product.<sup>3</sup>

The first example of application of the PT principle to iron carbonyl mediated organic transformations was the stoichiometric reduction of aromatic nitro compounds to amines under very mild conditions.<sup>4</sup> For the important reaction of carbonylation of organic halides,<sup>1</sup> the most useful iron carbonyl reagent proved to be the tetracarbonyliron dianion (2) usually prepared from pentacarbonyliron (1) under strictly anhydrous conditions (eq 1a).

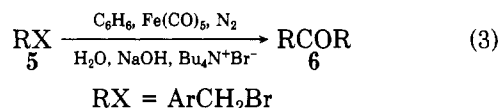


Further alkylation of 2, also conducted in an homogeneous dry medium followed by CO insertion, gives anions 3 (eq 1b). These anions can be stoichiometrically converted into aldehydes by protonation, ketones by alkylation, and carboxylic acids by oxidation.<sup>6</sup> We previously showed<sup>7</sup> that 2 could be transiently generated from pentacarbonyliron under mild PT conditions, although it is strongly hydrolyzed to give 4 in an homogeneous aqueous medium (eq 2, pK<sub>a</sub>(4/2) = 12–14<sup>8</sup>).



Prior to our work, Kimura et al. described in a short paper the stoichiometric carbonylation of organic halides with Fe(CO)<sub>5</sub> under PT conditions.<sup>9</sup> They found that benzyl bromides 5 could be stoichiometrically converted into ketones 6 provided that the aqueous concentration of sodium hydroxide is high enough (33%) (eq 3). Reaction with alkyl bromides RBr was more sluggish, but addition

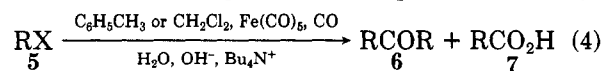
of a reactive alkyl iodide, R'I, finally gave unsymmetrical ketones, RCOR'.



No mechanistic study attempted to explain the results. We briefly mentioned in preliminary accounts<sup>10</sup> that, somewhat contrary to Kimura's results, benzyl halides could be catalytically carbonylated by Fe(CO)<sub>5</sub> under very mild PT conditions (in 1 M NaOH) to give either ketones or acids. Similar observations were published later by others,<sup>11</sup> although they reported inferior yields and gave no experimentally supported explanation of the results. We described the first mechanistic features of this reaction in a preliminary communication.<sup>12</sup> We now report full details of our studies of the catalytic carbonylation of organic halides with pentacarbonyliron under liquid-liquid PT conditions. In the first part, we examine the scope and the selectivity of the reaction. Then we describe a mechanistic and kinetic study of the PT carbonylation of benzyl bromide under various conditions.

## Results

**A. Scope and Selectivity of the PT Carbonylation of Organic Halides into Ketones or Acids. 1. Substrate.** Various benzyl halides can be converted either into ketones or acids as the major products, depending on the reaction conditions (eq 4; R = ArCH<sub>2</sub>, X = Cl, Br; by-



products 8–10; see Table I). Preliminary results showed that the aromatic ring can tolerate various substituents in the ortho, meta, or para positions or can be the naphthyl group.<sup>10</sup>

Less reactive alkyl halides were less successful, particularly with respect to the catalytic production of acids. For

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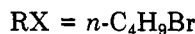
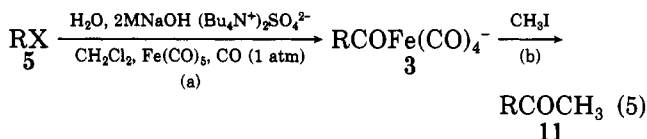
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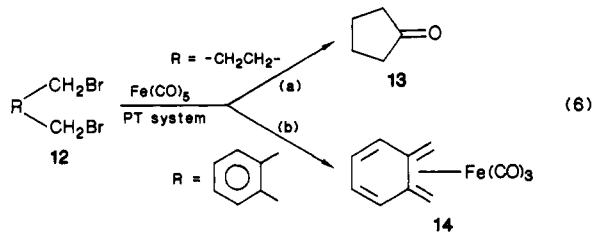
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instance, with a 0.5 volume-to-volume ratio of *n*-butyl bromide and dichloromethane as the organic phase, we observed a stoichiometric transformation of pentacarbonyliron into the acyltetracarbonyliron anion (3, eq 5a). This anion, present in the organic phase as a tetra-



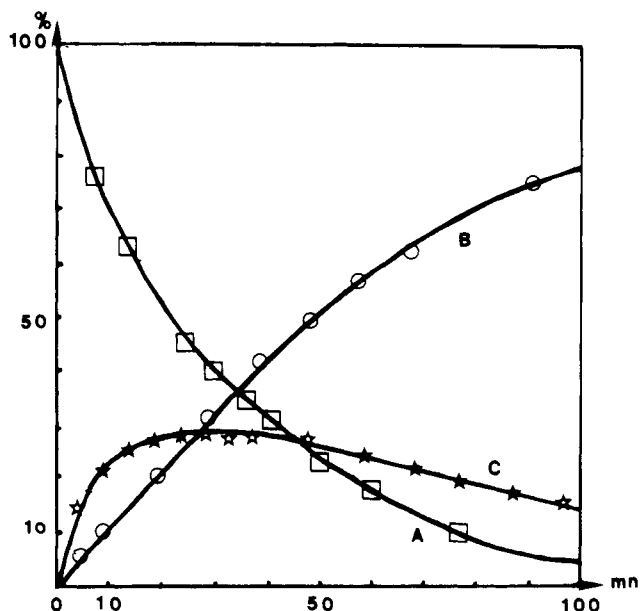
butylammonium salt, was identified by IR spectroscopy ( $\nu_{\text{C=O}}$  1995 (m), 1910 (sh), 1885 (s)  $\text{cm}^{-1}$ ;  $\nu_{\text{C-O}}$  1590 (m)  $\text{cm}^{-1}$ ) and by methylation to give the ketone (11, eq 5b, 80% yield vs  $\text{Fe}(\text{CO})_5$ ). Only traces of acid ( $\text{R} = \text{C}_4\text{H}_9$ ) could be detected in this run. Under the same conditions, 1,4-dibromobutane ( $\text{R} = -\text{CH}_2\text{CH}_2-$ ) directly gave cyclopentanone (200% yield vs  $\text{Fe}(\text{CO})_5$ , eq 6a). However,



$\alpha, \alpha'$ -dibromo-*o*-xylene gave in low yield the orthoquinodimethane complex 14 with no production of the cyclic ketone (eq 6b). Structural evidence for 14 was obtained by spectroscopy and agreed with published data (IR,<sup>13</sup> NMR,<sup>13</sup> MS). It is worth mentioning here that 14 could also be prepared in 35% yield by reaction of  $\alpha, \alpha'$ -dibromo-*o*-xylene with anion 2 under anhydrous conditions.<sup>14</sup>

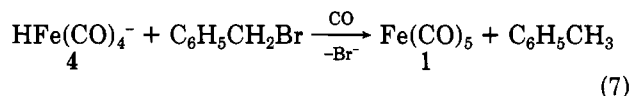
**2. Reaction Conditions and Selectivity.** Table I shows the most important factors governing the selectivity of the PT carbonylation of benzyl bromide, on which we will henceforth focus our attention. First, results of run 3 contrast strikingly with all others, since under those conditions the reaction is poor. It is also shown that the production of acid is favored by (i) a low  $\text{Fe}(\text{CO})_5/\text{RX}$  ratio (runs 1–12; this ratio can be as low as 1/50 as in run 2); (ii) carbon monoxide pressure (although an increase from 1 to 60 atm does not change very significantly the product ratios as in runs 1 and 4); and (iii) an excess of hydroxide in the aqueous phase (the greater excess does not influence the product ratios; runs 10 and 11). Conversely, the following factors strongly favor production of the ketone: (i) a low aqueous concentration of hydroxide (this is obtained by the use of saturated calcium hydroxide; runs 13–15); (ii) an inert atmosphere (then the reaction is not catalytic and the  $\text{Fe}(\text{CO})_5/\text{RX}$  ratio should be 1/2; run 14), and introduction of carbon monoxide pressure inhibits the production of ketone; (iii) a low stirring speed (compare runs 1, 7, and 8); and (iv) an increase in temperature (compare runs 1 and 5). So by a proper choice of experimental conditions, production of ketone can be made truly catalytic, although the selectivity remains modest (runs 5, 6, 8, and 15).

Run 12 shows that the same results can be obtained by replacing  $\text{Fe}(\text{CO})_5$  with the tetrabutylammonium salt of 3 ( $\text{R} = \text{C}_6\text{H}_5\text{CH}_2$ ). We also observed similar results with the tetrabutylammonium salt of 4. This last result is not surprising since a separate experiment showed that this



**Figure 1.** Rates of disappearance of benzyl bromide and appearance of the phenylacetate anion under PT conditions with  $\text{Fe}(\text{CO})_5$  as the catalyst precursor (conditions: 10 mmol of NaOH; 0.5 mmol of  $\text{Bu}_4\text{N}^+\text{HSO}_4^-$ ; 2.5 mmol of  $\text{PhCH}_2\text{Br}$ ; 0.25 mmol of  $\text{Fe}(\text{CO})_5$ ; 10 mL of  $\text{H}_2\text{O}$ ; 10 mL of  $\text{CH}_2\text{Cl}_2$ ; 1 atm of CO; 1200 rpm; 20 °C): curve A ( $\square$ ), %  $\text{PhCH}_2\text{Br}$  remaining (vs the initial quantity); curve B ( $\circ$ ), %  $\text{PhCH}_2\text{CO}_2^-$  produced (vs the initial quantity of  $\text{PhCH}_2\text{Br}$ ); curve C ( $\star$ ), %  $\text{PhCH}_2\text{Br}$  consumed – %  $\text{PhCH}_2\text{CO}_2^-$  produced.

anion reacted rapidly with benzyl bromide to give pentacarbonyliron and toluene quantitatively (eq 7); re-formed  $\text{Fe}(\text{CO})_5$  could reenter the catalytic cycles.



Finally, in run 4, we found that the amount of carbon dioxide produced after the end of the catalytic reaction almost equaled the amount of initial pentacarbonyliron.

**B. Kinetic Study of the Catalytic PT Carbonylation of Benzyl Bromide.** The water–dichloromethane two-phase system of run 4 (Table I) was chosen as a reference for this study. Due to the complexity of the system (multistep catalytic cycles in two different phases with important interfacial effects), we limited our investigations to an experimental kinetic study. In order to compare several runs, it is essential to state the geometry of the apparatus, the volumes of the two liquid phases, and the stirring speed (which is strongly correlated to the interfacial area)<sup>15</sup> as well as temperature and pressure. For kinetics at 1 atm of carbon monoxide, we used a thermostated glass cell described previously.<sup>16</sup> Kinetics at higher pressures were done in a thermostated stainless-steel autoclave. In all cases, the stirring rate was electronically monitored. The ratio of benzyl bromide (in percent vs the initial quantity) was determined by GC vs an internal standard. Scatter between three runs did not exceed  $\pm 4\%$ . An example of a plot of this ratio vs time is given on Figure

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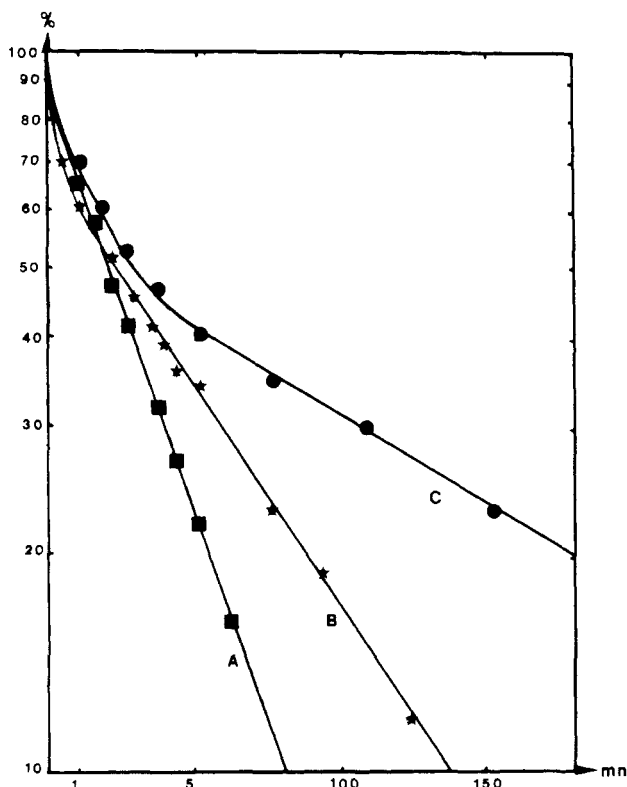
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**Table II. Pseudo-First-Order Kinetic Constants for the Rate of Disappearance of Benzyl Bromide under Various PT Catalytic Conditions**

entry	Bu <sub>4</sub> N <sup>+</sup> H <sub>2</sub> SO <sub>4</sub> <sup>-</sup> , mmol	NaOH, mmol	Fe(CO) <sub>5</sub> , mmol	t, °C	PCO, atm	stirring speed, rpm	10 <sup>4</sup> k <sub>obsd</sub> <sup>a</sup> s <sup>-1</sup>
1 <sup>b</sup>	0.5	10	0.25	20	1	1200	4.68
2	0.5	10	0.25	20	1	1000	2.35
3	0.5	10	0.25	20	1	800	1.07
4	0.5	20	0.25	20	1	1200	8.52
5	1	10	0.25	20	1	1200	5.67
6	0.25	10	0.25	20	1	1200	3.17
7	0.5	10	0.25	10	1	1200	2.98
8 <sup>c</sup>	0.5	15	0.25	20	1	1200	2.16
9	0.5	15	0.25	20	40	1200	2.33

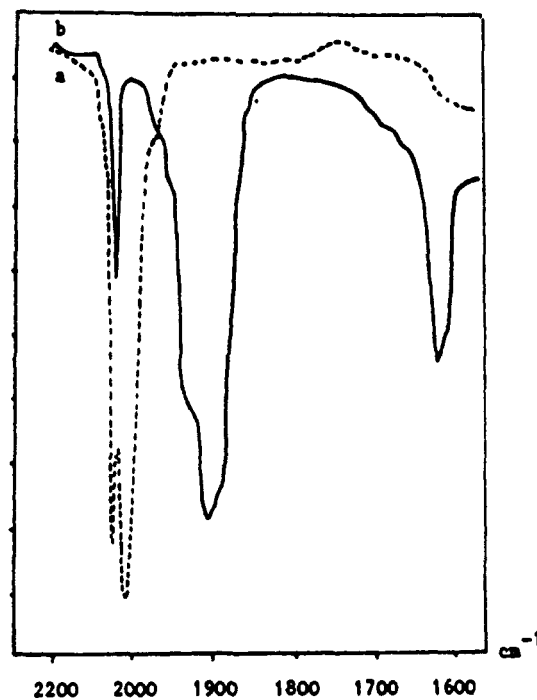
<sup>a</sup> Calculated as pseudo-first-order rate constants from the linear part of the semilog plot (see Figure 2 for examples). <sup>b</sup> Runs 1–7: apparatus, glass cell described in ref 16; liquid–liquid system, 10 mL of H<sub>2</sub>O/10 mL of CH<sub>2</sub>Cl<sub>2</sub>, 2.5 mmol of C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>Br. <sup>c</sup> Runs 8–9 (not comparable to runs 1–7): apparatus, autoclave (see Experimental Section); liquid–liquid system, 10 mL of H<sub>2</sub>O/15 mL of CH<sub>2</sub>Cl<sub>2</sub>, 3.75 mmol of C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>Br.



**Figure 2.** Semilog plot of the rate of disappearance of benzyl bromide under PT conditions with Fe(CO)<sub>5</sub> as the catalyst precursor for various stirring speeds [conditions: H<sub>2</sub>O/CH<sub>2</sub>Cl<sub>2</sub>, 10/10; NaOH, 10 mmol; Bu<sub>4</sub>N<sup>+</sup>H<sub>2</sub>SO<sub>4</sub><sup>-</sup>, 0.5 mmol; PhCH<sub>2</sub>Br, 2.5 mmol; Fe(CO)<sub>5</sub>, 0.25 mmol; 20 °C; 1 atm of CO]: curve A (■), 1200 rpm stirring; curve B (★), 1000 rpm stirring; curve C (○), 800 rpm stirring.

1 (curve A) for the experimental conditions of run 4, Table I. The rate of acid appearing as the phenylacetate anion in the aqueous phase was also determined by UV spectrophotometry at 258 nm and expressed in percent vs the initial quantity of benzyl bromide. Its plot vs time is also given in Figure 1 (curve B). Curve C of Figure 1 shows the change in the ratio of benzyl bromide to phenylacetate anion. This change is large from the beginning of the reaction, where it correlates with the initial reaction rates estimated from the initial slopes of curve A (10%/min) and curve B (5%/min).

A semilog plot of the rate of remaining benzyl bromide vs time is given in Figure 2 (curve A) for the experimental conditions of run 4, Table I. It shows pseudo-first-order behavior after a short induction period. Pseudo-first-order rate constants are given in Table II for various experimental conditions. Table II shows the kinetic effect of

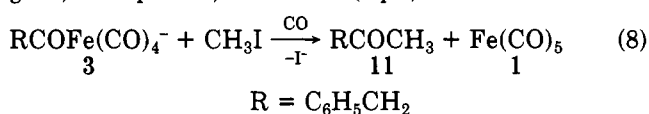


**Figure 3.** IR spectra taken from the organic phase (a) at the beginning and (b) at the end of the catalytic carbonylation of benzyl bromide.

several important factors (their effects on the product ratios have been highlighted in Table I). A slower stirring speed strongly affects the rate of the reaction (curves A–C, Figure 2, and entries 1–3, Table II), and, as shown in Table I, the product ratios. The kinetic effect of temperature is also noticeable in the range 10–20 °C ( $k_{\text{obsd}}(20\text{ °C})/k_{\text{obsd}}(10\text{ °C}) = 1.57$ ) without significant modification of the yield of acid 7 (73%). Recall that an increase to 30 °C strongly decreases this yield (39%, run 6, Table I). The rate of the reaction also increases with an increase in the ratio of the cationic carrier (runs 1 and 5, Table II) to the hydroxide anion (entries 1 and 4, Table II). An increase in the carbon monoxide pressure from 1 to 40 atm does not have any significant kinetic effect (entries 8 and 9, Table II).

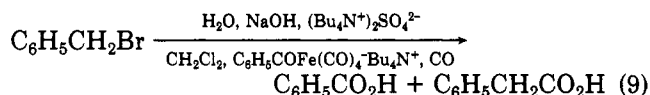
**C. IR and Chemical Evidence for the Role of the Acyltetracarbonyliron Anion RCOFe(CO)<sub>4</sub><sup>-</sup> (3) in the PT Catalytic Carbonylation of Benzyl Bromide into Ketone 6 or Acid 7.** IR examination of the organic layer was undertaken under 40 atm of CO in a stainless-steel autoclave at 25 °C and a 1200 rpm stirring rate (10 mL of H<sub>2</sub>O, 15 mL of CH<sub>2</sub>Cl<sub>2</sub>, 15 mmol of NaOH, 0.5 mmol of Bu<sub>4</sub>N<sup>+</sup>H<sub>2</sub>SO<sub>4</sub><sup>-</sup>, 3.75 mmol of benzyl bromide, 0.25 mmol of Fe(CO)<sub>5</sub>). Figure 3 shows the spectra taken at the be-

ginning and at the end of the reaction, a mixed spectrum being observed in the middle of the reaction. At the end of the reaction, pentacarbonyliron has completely disappeared, and the new appearing bands were found to be fully consistent with those quoted in literature for anion 3 ( $R = C_6H_5CH_2$ ).<sup>17</sup> Further methylation (MeI) rapidly gave, as expected, ketone 11 (eq 8).<sup>17</sup> The amount of

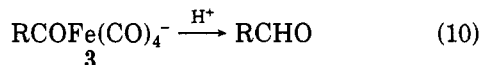


$Fe(CO)_5$  produced in eq 8 was found to be equivalent to the amount of  $Fe(CO)_5$  introduced in the catalytic PT system. Reaction 8 also explains why an IR spectrum taken in the middle of the catalytic reaction still shows the presence of  $Fe(CO)_5$ ; this is due to a rapid reaction of benzyl bromide, then in excess, with anion 3 in the organic phase withdrawn for the IR examination.

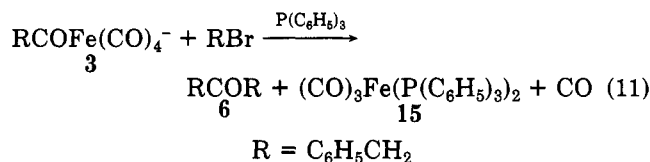
In order to gain further insight into the role of in situ generated 3 in the catalytic reaction, we designed a crossover experiment. Anion 3 ( $R = C_6H_5$ ) was prepared as a tetrabutylammonium salt according to a known procedure<sup>17</sup> and added to a PT system (10 mL of  $H_2O$ , 10 mL of  $CH_2Cl_2$ , 10 mmol of NaOH, and 0.5 mmol of  $Bu_4N^+HSO_4^-$  at  $+10^\circ C$  under 10 atm of CO). After 1 h, no benzoic acid was detected in the aqueous phase, and no change in concentration of this salt was detectable by IR examination of the organic layer. Introduction of 1.25 mmol of benzyl bromide (at a 1200 rpm stir rate) immediately started the catalytic reaction shown in eq 9.



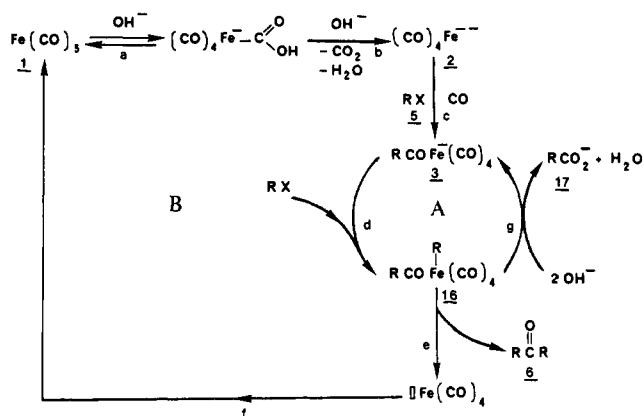
After the disappearance of benzyl bromide (GC), benzoic acid and phenylacetic acid were extracted from the aqueous layer ( $C_6H_5CO_2H$ , 40% vs initial quantity of 3 ( $R = C_6H_5$ );  $C_6H_5CH_2CO_2H$ , 80% vs initial quantity of benzyl bromide). Acidification of the organic layer (glacial acetic acid) gave  $C_6H_5CHO$  and  $C_6H_5CH_2CHO$  in 15–85% yields, respectively. This indicates that both anions 3 ( $R = C_6H_5$  and  $R = C_6H_5CH_2$ ) were present in the organic phase at the end of the reaction and trapped as aldehydes according to the well-known reaction (10).<sup>17</sup>



The effect of an external ligand was also examined. Under the experimental conditions of run 9 (Table II), a sample of the organic layer was quickly withdrawn from the autoclave when the reaction was half finished, and immediately quenched with an excess of triphenylphosphine. An IR spectrum showed the presence of  $(CO)_3Fe(P(C_6H_5)_3)_2$  (15,  $\nu_{C=O}$  1880 (s)  $cm^{-1}$ ) with traces of  $(CO)_4FeP(C_6H_5)_3$  (16, detected by its main absorption band at 1947  $cm^{-1}$ ). The presence of both 15 and 16 along with 6 ( $R = C_6H_5CH_2$ ) was confirmed by TLC. The reaction is shown in eq 11.



**Scheme I. The Two Competing Catalytic Cycles of Carbonylation of Benzyl Bromide under PT Conditions with  $Fe(CO)_5$ : Cycle A for the Production of the Phenylacetate Anion and Cycle B for the Production of Diphenylpropanone**



### Discussion

The results clearly show that two main competing catalytic cycles occur during the PT carbonylation of benzyl bromide with  $Fe(CO)_5$ , one giving the acid (7) and one giving the ketone (6).<sup>19</sup> We feel that the two catalytic cycles A and B given in Scheme I account for the observed results. We demonstrated previously that 3 ( $R = C_6H_5CH_2$ ) could be generated from 1 and 5 under PT conditions, most likely through the transient PT generation of very reactive 2<sup>7</sup> (Scheme II, steps a and b). Curves A in figures 1 and 2 show that, apparently, there is no induction period for the catalytic process: stirring immediately causes the disappearance of benzyl bromide and the production of phenylacetic acid, although the initial rates are very different,  $\sim 10\%/min$  for the former and  $\sim 5\%/min$  for the latter.  $Fe(CO)_5$  ( $Fe(CO)_5/RX$  initial ratio = 1/10) should be consumed in less than 2 min to give organosoluble organometallic derivatives. One of them, as shown above, is certainly 3, maintained in dichloromethane as a tetrabutylammonium salt. Meanwhile, and for a few minutes after this time, the rate of disappearance of benzyl bromide is still rapid, although the production of 7 remains modest. This can be interpreted by assuming that benzyl bromide reacts with 3 to give unstable  $RCOFe(CO)_4R$  (16, Scheme I). Such an intermediate has been postulated already in the synthesis of ketones  $RCOR'$  by the reaction of halides with 3.<sup>20</sup> The production of an acid (as the carboxylate anion 17) is then accounted for by the catalytic cycle A (Scheme I), in which it is shown that anion 17 comes from a base-catalysed cleavage of 16. There are precedents in the literature for base-catalysed cleavage of transition-metal acyl organometallic derivatives.<sup>21</sup> Support for such a cleavage is given by the crossover experiment designed in eq 9. Production of both acids ( $R = C_6H_5$  and  $C_6H_5CH_2$ ) is explained by the equilibria and base-catalysed cleavages shown in eq 12 that give both anions  $RCOFe(CO)_4^-$  (3,  $R = C_6H_5$  and  $C_6H_5CH_2$ ). The competing catalytic production of ketone

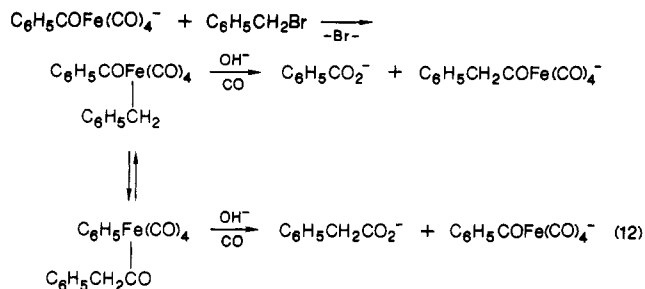
(19) Small amounts of 8 could be ascribed to a reductive elimination of  $R_2Fe(CO)_4$ , which is probably in equilibrium with  $RCOFe(CO)_4R$  (16). Ester 10 is produced by PT reaction between the phenylacetate anion and benzyl bromide.

(20) Reference 6 and: Collman, J. P.; Finke, R. G.; Cawse, J. N.; Brauman, J. I. *J. Am. Chem. Soc.* 1977, 99, 2515; 1978, 100, 4766.

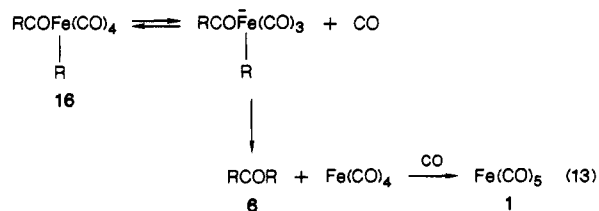
(21) A close example is the base-catalysed cleavage of acylpentacarbonylmanganese to give a carboxylic acid, carefully studied by: Johnson, R. W.; Pearson, R. G. *Inorg. Chem.* 1971, 10, 2091. Other references on the base catalysed cleavage of transition-metal acyl complex are available in ref 1c, p 406.

(17) Siegl, W. O.; Collman, J. P. *J. Am. Chem. Soc.* 1972, 94, 2516.

(18) (a) Clifford, A. F.; Mukherjee, A. K. *Inorg. Synth.* 1966, 8, 185. (b) Reckziegel, A.; Bigorgne, M. *J. Organomet. Chem.* 1965, 3, 341.



is described in the catalytic cycle B (Scheme I). It shows that carbon monoxide is incorporated twice, in steps c and f, consistent with the production of 15 when triphenylphosphine is introduced. The directing of the catalytic processes toward the production of 6 or 7 as the dominant species can be understood fairly well. The catalytic cycle A (giving the acid 7) is favored by every factor that increases the rate of the base-catalyzed cleavage of the intermediate 16 (an increase in the stirring speed, the aqueous concentration of the hydroxide anion, or the amount of the cationic carrier). Factors that decrease this rate should favor the production of ketone. Production of ketone is also favored by an increase in temperature and an inert atmosphere. This is consistent with reductive elimination from 16, which should be initiated by prior decooordination of carbon monoxide (eq 13). A CO at-

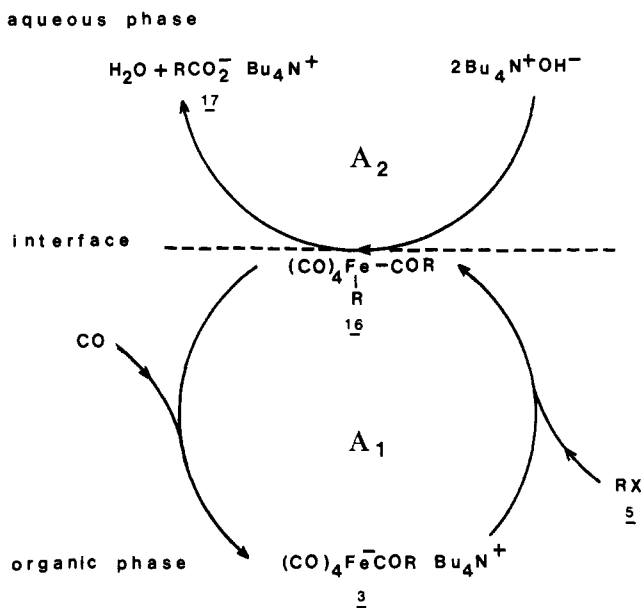


mosphere exerts an inhibiting effect on the production of ketone 6, consistently with current ideas about reductive elimination processes on many organometallic derivatives, which need prior decooordination of an auxiliary ligand.<sup>22</sup>

Cycles A and B of Scheme I also explain why in eq 5 the process of carbonylation of butyl bromide stops after the production of 3: butyl bromide is not reactive enough to give 16 (Scheme I) and, subsequently, ketone 6 or the carboxylate anion 17.

An important feature of this PT catalytic system is the liquid-liquid interface. Since the ion pair  $\text{Bu}_4\text{N}^+\text{OH}^-$  is not extractable into the organic phase,<sup>23</sup> reactions involving hydroxide should occur at the interface. A structure of the interfacial zone has been proposed in a previous paper in which the important steps a and b (Scheme I) are also discussed.<sup>7b</sup> The role of the interfacial area is also important in the directing the reaction toward ketone 6 or anion 17: an increase in area increases the rate of production of acid 7, as shown in Table I (runs 4, 7, and 8). Kinetic results of Table II (entries 1, 5, and 6) show that the base-catalyzed cleavage of 16 (see Scheme II) by hydroxide is assisted by the tetrabutylammonium cation; this step also should occur at the interface. Another important consequence of the existence of two immiscible phases is the automatic separation of the catalyst 3, which is found in the organic phase as a tetrabutylammonium salt, and the acid product 7, which is expelled as the water-soluble anion 17 into the aqueous phase. The organic phase can be reused for other catalytic runs.

### Scheme II. The Two Parts of the Catalytic Cycle A (Production of the Phenylacetate Anion) in the Two-Phase System



### Conclusion

We have shown in this work that carbonylation of benzyl halides to give ketones or carboxylic acids can be made catalytic with pentacarbonyliron under liquid-liquid PT conditions. We have also demonstrated that the acyl-tetracarbonyliron anions,  $\text{RCOFe}(\text{CO})_4^-$ , generated in situ through a rapid reaction of benzyl halides on the transiently PT generated anion  $\text{Fe}(\text{CO})_4^{2-}$ , are as good as (or better than) the well-known tetracarbonylcobalt anion for the catalytic carbonylation of benzyl halides.<sup>24</sup> Whether ketones or acids are produced depends on the fate of the postulated intermediate  $\text{RCOFe}(\text{CO})_4\text{R}$ : a reductive elimination process gives the ketone, while a competing base-catalyzed cleavage gives the acid.

### Experimental Section

**General Methods.** All reactions were carried out under a nitrogen or carbon monoxide atmosphere. Reactions at atmospheric pressure of nitrogen or carbon monoxide were run in a round-bottom Schlenk tube (apparatus A) (diameter 40 mm) surrounded by a thermostated jacket (circulation Lauda thermostat,  $\pm 0.1^\circ\text{C}$ ), equipped with a rubber septum capped sidearm, and connected to a vacuum nitrogen or carbon monoxide line. Reactions under pressure of carbon monoxide were run in a stainless-steel autoclave (apparatus B) whose interior diameter was fitted for the reception of a round-bottom glass tube (of 40-mm external diameter), equipped with a valve for the introduction of reagents and a valve for the withdrawing of samples from the organic phase and connected to a pressure line (nitrogen or carbon monoxide); a thermostated jacket secured stable temperature (Lauda thermostat,  $\pm 0.1^\circ\text{C}$ ). For both apparatus A and B, stable stirring was provided by introducing a "Baroval" magnetic bar fitting the round-bottom of the glass tube and driven by an electronically monitored combimag stirring plate ( $\pm 50$  rpm maximum drift).

<sup>1</sup>H NMR spectra were recorded with a Varian EM 360 spectrometer. Infrared spectra were recorded with a Philips UNICAM SP 1100 spectrometer. UV spectrophotometric analyses were recorded with an Hitachi UV-visible spectrophotometer. GC analyses were carried out with an Intersmat ICG 1200 DFL FID

(22) A general discussion on this problem is available in ref 1c, p 322.

(23) Rabinovitz, M.; Cohen, Y.; Halpern, M. *Angew. Chem., Int. Ed. Engl.* 1986, 25, 960.

(24) This catalyst-product separation was also observed in our previous study of the PT carbonylation of benzyl bromide with the large and lipophilic anion  $\text{Co}(\text{CO})_4^-$ ,<sup>14</sup> which is otherwise much less efficient than the present one under comparable conditions.

model gas chromatograph interfaced with a 3390 A Hewlett-Packard integrator and fitted with a 1-m column of Apiezon (on Chromosorb HMDS).

**Materials and Solvents.** Organic halides and GC internal standards were purchased from Aldrich Co., distilled, and checked for purity (GC and NMR) prior to use. Pentacarbonyliron, tetrabutylammonium hydrogen sulfate, analytically pure sodium hydroxide, and calcium hydroxide were used as received from Aldrich Co. Water was distilled twice under nitrogen. Organic solvents, of analytical grade (dichloromethane, toluene), were distilled under nitrogen. Anions **3** ( $R = C_6H_5, C_6H_5CH_2$ ) were prepared as sodium or tetrabutylammonium salts according to a procedure derived from the one described in ref 17.

**Identification of Compounds 6–10:** GC (except for **7**), IR, and  $^1H$  NMR, by comparison with authentic samples.<sup>25</sup>

**Carbon Dioxide:** volumetric analysis after acidification (HCl) of the aqueous phase.<sup>7b</sup>

**PT Synthesis of Anion 3 [ $RCOFe(CO)_4^-$ ] and Ketone 11 ( $RCOCH_3$ ,  $R = n-C_4H_9$ ).** The following reagents and solvents were introduced, under a carbon monoxide atmosphere into apparatus A: 1 mmol of  $Bu_4N^+HSO_4^-$ , 15 mL of 2 M aqueous NaOH, 5 mL of  $CH_2Cl_2$ , 2.5 mL of  $n-C_4H_9Br$ , and 1 mmol of  $Fe(CO)_5$ . The mixture was stirred at 1200 rpm for 3.5 h at room temperature under 1 atm of carbon monoxide. An IR spectrum taken from the organic layer showed the disappearance of  $Fe(CO)_5$  and characteristic bands of anion **3** (as a tetrabutylammonium salt:  $\nu_{C=O}$  1995 (m), 1910 (sh), 1885 (s)  $cm^{-1}$ ;  $\nu_{C-O}$  1590 (m)  $cm^{-1}$ ). Further methylation (MeI) quickly gave ketone **11** in 80% molar ratio vs  $Fe(CO)_5$  (determined by GC with cyclopentanone as the internal standard).

**PT Synthesis of Cyclopentanone.** A similar procedure to the previous one was used, with the same proportions of reagents but with 1,4-dibromobutane in the place of  $n$ -bromobutane. The reaction was run at room temperature for 14 h and at +50 °C for an additional 5 h. The in situ yield into cyclopentanone was determined by GC (internal standard, cyclohexanone): 200% molar ratio vs  $Fe(CO)_5$ .

**PT Synthesis of the (Orthoquinodimethane)triacarbonyliron (**14**).** The following reagents and solvents were introduced into apparatus A under a nitrogen atmosphere: 12.5 mmol of NaOH, 0.5 mmol of  $Bu_4N^+HSO_4^-$ , 2 mmol of  $\alpha, \alpha'$ -dibromo-*o*-xylene, 10 mL of  $H_2O$ , 10 mL of toluene, 25 °C, stirring speed 1200 rpm.  $Fe(CO)_5$  (1 mmol) was then added slowly by syringe through a rubber septum (3 h). The in situ yield was determined by the NMR technique after the introduction of a known amount of anisole as an internal standard (13–20% vs  $Fe(CO)_5$ ). Complex **14** can be separated from toluene and by-products by evaporation in vacuo and trapping of the vapors in a small Schlenk tube plunged in liquid nitrogen. Spectral data:<sup>13</sup> MS calcd for  $C_{11}H_8FeO_3$  243.9822, found 243.9843; IR (hexane,  $cm^{-1}$ )  $\nu_{C=O}$  2057 (sharp, s), 1987 (sharp, s);  $^1H$  NMR (solvent  $CD_3COCD_3$ ,  $\delta$  vs external TMS) 0.32 (d, 2 H), 2.53 (d, 2 H,  $J = 3$  Hz); 7.5 (m, 4 H).

**PT Carbonylation of Benzyl Halides into Ketones **6** or Acids **7**.** Apparatus A was used for carbonylations at atmospheric

pressure, with the temperature of the cell fixed at the desired value, and the cell purged by several vacuum–nitrogen-filling cycles. Then the exact amounts of solid reagents were introduced ( $NaOH$  or  $Ca(OH)_2$ ,  $Bu_4N^+HSO_4^-$ ) and the cell purged again and filled with carbon monoxide (or nitrogen). Suitable volumes of water and organic solvent were injected through the rubber septum, and then the benzyl halide was injected. After a short time of stirring, the exact volume of pentacarbonyliron was introduced by injection, and the stirring speed set at the desired value. At the end of the reaction (no benzyl halide detected by GC), stirring was stopped, and after decantation, the aqueous phase was withdrawn and acidified (HCl) and the acid **6** extracted with diethyl ether. The ethereal extracts were dried, evaporated to dryness, checked for purity by  $^1H$  NMR. The organic phase was analyzed by GC and evaporated for an  $^1H$  NMR analysis of the mixture. Yields of acids **6** were determined by weight and yields of **5**, **7**, **8**, and **9** by  $^1H$  NMR or GC (with convenient internal standards), depending on the volatility of the mixture. Apparatus B was used for reactions under carbon monoxide pressure. The autoclave was purged by several one atmosphere–40 atm nitrogen-filling cycles. The reagents (pure liquids or in liquid solutions) were introduced through a valve under a nitrogen stream. Then carbon monoxide was introduced and the pressure raised to the desired value. A sidearm equipped with a valve and connected to a tube extending into the organic phase (when stirring was stopped) allowed samplings of the organic phase for monitoring of the reaction. The workup of the reaction was the same as described above.

**Kinetic Measurements.** The rate of disappearance of benzyl bromide was measured by GC. Prior to the injection of pentacarbonyliron, a suitable amount of naphthalene (1 mmol for 1 mmol of benzyl bromide used) was introduced in the apparatus as an internal standard. Stirring for several minutes secured the thermal equilibrium of the mixture. Stirring was stopped, pentacarbonyliron was injected, and the carbon monoxide pressure was immediately raised to the fixed value (when apparatus B was used); a sample withdrawn from the organic layer and injected in the GC apparatus gave the 100% value of the concentration of benzyl bromide. Then stirring was started, and this time was taken as the zero time for kinetics. Every 5 or 10 min, stirring was stopped for a short time to withdraw a sample from the organic layer, which was injected immediately into the GC apparatus. Analytical results were obtained in less than 5 min. The reaction was monitored up to at least 85% consumption of benzyl bromide. At least three runs were made at one set of experimental conditions. Scatter between measurements for the same time were found to be less than  $\pm 4\%$ . Analytical data were processed according to the linear regression method to give the pseudo-first-order constants  $k_{obsd}$  of Table II. Correlation coefficients were better than 0.99. In runs 2 and 3 of Table I,  $k_{obsd}$  was determined graphically on the linear part of the semilog adjustment (Figure 2).

The rate of appearance of the phenylacetate anion was measured spectrophotometrically at 258 nm every 5 or 10 min after the stirring was stopped for a short time. Scatter between several runs for one time were less than  $\pm 4\%$ .

**Registry No.** **14**, 12181-95-2;  $Fe(CO)_5$ , 13463-40-6;  $PhCH_2Br$ , 100-39-0;  $Bu_4N^+HSO_4^-$ , 32503-27-8;  $n-C_4H_9Br$ , 109-65-9; 1,4-dibromobutane, 110-52-1;  $\alpha, \alpha'$ -dibromo-*o*-xylene, 91-13-4.

(25) (a) Pouchert, C. J. *The Aldrich Library of NMR Spectra*, 2nd ed.; Milwaukee, 1983. (b) Pouchert, C. J. *The Aldrich Library of IR Spectra*, 3rd ed.; Milwaukee, 1981.