20a, 89555-89-5; **21**, 89555-91-9; **22**, 89555-93-1; **23**, 89555-94-2; **24**, 89530-52-9; **25**, 89530-53-0; **27**, 89555-82-8; **29**, 82639-77-8; **30**, 89555-96-4; **31**, 89555-97-5; **32**, 89555-98-6; **34**, 89555-99-7; **36**, 89556-00-3; **45**, 10170-53-3; (*R**,*R**)-4-methylhex-5-en-2-ol, 71228-22-3; (*R**,*S**)-4-methylhex-5-en-2-ol, 71228-23-4; (*R**,*R**)-3-methylhex-5-en-2-ol, 1499-66-7; (*R**,*S**)-3-methylhex-5-en-2-ol, 1695-93-8; (4-methylpent-4-enyl)bis(dimethylglyoximato)(pyridine)cobalt(III), 89530-45-0; (2-methyl-4-enyl)bis(dimethylglyoximato)(pyridine)cobalt(III), 89530-46-1; hex-5-en-2-ylbis(dimethylglyoximato)(pyridine)cobalt(III), 89530-47-2; (5-methylhex-5-en-2-yl)bis(dimethylglyoximato)(pyridine)cobalt(III), 89530-48-3; (*R**,*R**)-(4-methylhex-5-en-2-yl)bis(dimethylglyoximato)(pyridine)cobalt(III), 89530-49-4; (*R**,*S**)-(4-methylhex-5-en-2-yl)bis(dimethylglyoximato)(pyridine)cobalt(III), 89614-94-8; (*R**,*R**)-(3-methylhex-5-en-2-yl)bis(dimethylglyoximato)(pyridine)cobalt(III), 89530-50-7; (*R**,*S**)-(3-methylhex-2-en-2yl)bis(dimethylglyoximato)(pyridine)cobalt(III), 89614-95-9; (6-methylhept-5-en-2-yl)bis(dimethylglyoximato)(pyridine)cobalt(III), 89530-51-8; pent-4-enylbis(dimethylglyoximato)(pyridine)cobalt(III), 36630-47-4; 2-(β,β,β-trichloroethyl)sulfolane, 82639-78-9; 3-chloro-1,1-dioxothiacyclohexane, 38690-82-3; 4,6,6,6-tetrachlorohexanesulfonyl chloride, 89555-79-3; 2-methyl-2-(β,β,β-trichloroethyl)sulfolane, 89555-81-7; *sec*-butylbis(dimethylglyoximato)(pyridine)cobalt(III), 54712-55-9; cyclohexylbis(dimethylglyoximido)(pyridine)cobalt(III), 28206-03-3; pent-4-enol, 821-09-0; hex-5-en-2-ol, 626-94-8; 2-methylpent-4-enol, 5673-98-3; 4-methylpent-4-enol, 22508-64-1; 6-methylhept-5-en-2-ol, 1569-60-4; 5-methylhex-5-en-2-ol, 50551-88-7; allyl bromide, 106-95-6; allyl alcohol, 107-18-6; 3-methyl-5-en-2-one, 2550-22-3; dimethylglyoxime, 95-45-4; trichloromethanesulfonyl chloride, 2547-61-7; oct-1-ene, 111-66-0; cyclooctene, 931-88-4; hexa-1,5-diene, 592-42-7; hepta-1,6-diene, 3070-53-9; *cis*,*cis*-1,5-cyclooctadiene, 1552-12-1; 3,3,3-trichloropropyl, 6565-20-4; sulfur dioxide, 7446-09-5; $CoCl_2$, 7646-79-9.

Catalytic Uses of $Fe(CO)_5$: Formation of Carboxylic Acid Derivatives

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Carboxylic acid derivatives were prepared by carbonylating an alkyl or aralkyl halide in the presence of a catalytic amount of iron carbonyl, a base, and an alcohol or water.

Although iron pentacarbonyl, $Fe(CO)_5$, is one of the most ubiquitous and least expensive metal carbonyls, few catalytic uses have been found for it. This is largely attributable to the difficulty associated with removal of a CO ligand to generate a site of coordinative unsaturation. Most of the catalytic uses of $Fe(CO)_5$ where CO is used as one of the reactants employ a base to chemically activate the CO ligand by converting it to CO_2, as follows:

$$\underset{\mathbf{1}}{Fe(CO)_5} + OH^- \rightarrow \underset{\mathbf{2}}{HFe(CO)_4^-} + CO_2$$

The anion **2** is the species that initiates the catalysis. The most famous example of this catalysis is the Reppe reaction whereby an olefin is treated with CO and water to form the next higher alcohol.[1] Pettit and others have applied this catalytic system in the hydroformylation of olefins,[2] aldehyde and ketone hydrogenation,[3,4] water gas shift reaction,[2,5] and the reduction of nitro compounds.[6] In these reactions $Fe(CO)_5$ is continuously being regenerated and remains an integral part of the catalytic cycle. Examples are also known where $Fe(CO)_5$ is used as a catalyst precursor in reactions where CO is not a reactant. In these cases $Fe(CO)_5$ usually does not reappear in the catalytic cycle. Thus, extremely active olefin isomerization and hydrosilation catalysts result from the removal of CO from $Fe(CO)_5$ by photolysis.[7] Back-reaction of CO destroys the coordinatively unsaturated species produced in these reactions, and catalysis stops when the light is turned off. Activation of $Fe(CO)_5$ can also be accomplished thermally, but again $Fe(CO)_5$ is removed from the catalytic cycle.[8]

Numerous stoichiometric carbonylation reactions have utilized $Fe(CO)_5$, usually in a reduced form. Probably the most well-known examples are those developed by Collman et al., where an alkyl halide is reacted with $Fe(CO)_4^{2-}$ in a stoichiometric reaction and then in a second step is converted to aldehyde, ketone, acid, ester, or hydrocarbon by the addition of the appropriate reagents.[9] In a related stoichiometric process investigated by Tsutsumi and coworkers, ketones and aldehydes were synthesized by reacting $Fe(CO)_5$ with organolithium reagents. The resulting lithium acyl carbonyl ferrate was then reacted with alkyl halides or protons, respectively.[10,11]

Here we report another catalytic process that uses the combination of $Fe(CO)_5$, base, CO, and hydroxylic solvent. The other reactant in this case is an alkyl or aralkyl halide, and the product is a carboxylic acid derivative:

$$RX + CO + R'OH \xrightarrow[\text{base}]{Fe(CO)_5} RC(O)OR'$$

The reactions typically occur under the mild conditions

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of 1 atm of CO and room temperature. There are actually two variants of this reaction. In one version, alcohol is the solvent and K_2CO_3 is the base; and esters are produced. Thus benzyl bromide and methanol produce methyl phenylacetate:

$$\underset{\mathbf{3}}{PhCH_2Br} + CO + MeOH \xrightarrow[K_2CO_3]{Fe(CO)_5} \underset{\mathbf{4}}{PhCH_2C(O)OCH_3}$$

In the other version, water is the hydroxylic component, a phase-transfer catalyst is present, NaOH is the base, and carboxylic acids are produced upon workup as illustrated in the synthesis of phenylacetic acid:

$$\underset{\mathbf{5}}{PhCH_2Cl} + CO + H_2O \xrightarrow[\substack{\text{hexane, NaOH,} \\ Fe(CO)_5}]{PhCH_2(C_2H_5)_3NCl} \underset{\mathbf{6}}{PhCH_2C(O)OH}$$

The turnovers in iron are limited to about 16, with 6 to 10 being a typical range for both of the reaction variants.

Of the two variations, the preferred one is the ester synthesis. Higher rates can be achieved, there are fewer byproducts, and sometimes $Fe(CO)_5$ can be isolated at the end of the reaction. Detailed in Table I are several examples of the ester synthesis. Run 1 exemplifies the most convenient and efficient way to perform the methyl phenylacetate synthesis.

Runs 2–5 show the effect of added cosolvents; the ether byproduct increases when *N*-methyl-2-pyrrolidone and acetonitrile are present. Benzyl chloride is a suitable substrate when activated by KI (run 6). Butyl iodide is a suitable substrate (run 7), but the rate of reaction is slower and roughly parallels the difference in substrate susceptibility to nucleophilic attack. Ethanol is also a suitable alcohol (run 8).

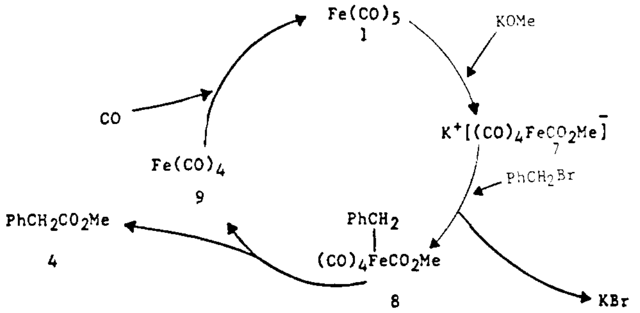
A series of experiments designed to examine the effect of pressure on turnover number was performed (runs 9–11). These systems were examined at lower levels of $Fe(CO)_5$ as reflected in the ester yield. Although the effect is not great, an increase in pressure does increase the number of turnovers in iron. There does not appear to be any advantage in working at pressures above 1000 psi.

Of the several different bases examined (K_2CO_3, Na_2CO_3, Li_2CO_3, KOH, NaOH, NaOMe), K_2CO_3 is by far the best. Yields of byproduct ether increase when strong soluble bases are added, although ether formation was lessened by adding the base at a slow rate. Benzyl alcohol is not produced in the presence of hydroxide. Apparently when K_2CO_3 is present, the amount of base actually in solution is small,

$$K_2CO_3 + CH_3OH \rightleftarrows KOCH_3 + KHCO_3$$

and $Fe(CO)_5$ is a better electrophile than benzyl halide. As long as the amount of free base is less than the amount of $Fe(CO)_5$, ether formation does not occur.

Examination of a methanolic solution of $Fe(CO)_5$ over K_2CO_3 by infrared spectroscopy reveals quantitative conversion to a species that we propose [because of its absorptions at 2008 (w), 1895 (s, br), and 1640 (m) cm^{-1}] to be the carbomethoxy anion $K[(CO)_4FeCO_2Me]$. This assignment is consistent with previous observations of carbomethoxy metal carbonyl anions[12] and distinguishable from the $[HFe(CO)_4^-]$ by the presence of the carbomethoxy band at 1640 cm^{-1} and the absence of the 1910-cm^{-1} band characteristic of the hydride.[13] The bis(triphenylphosphine)iminium (PPN) salt of this anion may be isolated from the methanol solution via metathesis and crystallization to yield $PPN[(CO)_4FeCO_2Me]$ with an IR spectrum as previously reported. Such a carbalkoxy anion has been proposed by Watanabe and co-workers as an intermediate in the stepwise stoichiometric carbalkoxylation of alkyl halides with $Fe(CO)_5$ and sodium alkoxides.[14] The formation of $[(CO)_4FeCO_2Me]^-$ by the reaction of methoxide with $Fe(CO)_5$ has also been observed by Pearson and Mauermann.[15] The catalytic formation of ester products may proceed as follows:



Collman and Siegl have studied the chemistry of anions of the type $[(CO)_4FeC(O)R]^-$ and have observed that they react with alkyl halides to yield ketones;[16] this provides some precedent for the **7** → **8** → **9** transformation proposed. Reductive elimination of ester from **8** generates the intermediate $Fe(CO)_4$, **9**, which is sufficiently unstable to remove some of the iron from the catalytic cycle. The observation that high CO pressures increase the number of catalyst turnovers supports this hypothesis.

The related phase-transfer process yielding acids is not as well understood as the ester synthesis. Several examples are detailed in Table II. Most reactions were run until noticeable CO uptake had stopped. Comparison of runs 1 and 2 illustrates the detrimental effect of heating the reaction. Replacement of benzyl chloride with benzyl bromide (run 3) causes the production of less phenylacetic acid but facilitates the formation of the interesting byproduct ketone $[PhCH_2CHPh]_2CO$ (**10**). Use of the nonpolar cosolvent hexane increases the yield of acid (run 4) and further increases in yield result from the use of higher levels of phase-transfer agent (run 5). Phase-transfer agent levels above 10 mol % of the benzyl halide promote hydrolysis to benzyl alcohol. Toluene is also a good cosolvent for the reaction (run 6), but CH_2Cl_2 is not (run 7).

Base concentration is an important variable; when concentrated base is used (run 8), the acid synthesis stops, and the ketone **10** is the product. More dilute base (run 9) lowers the rate. $Fe_2(CO)_9$ (run 10) and $Fe_3(CO)_{12}$ (run 11) can replace $Fe(CO)_5$ as catalyst precursors. Comparison of run 12 with run 1 reveals the beneficial effect of increased pressure, although the effect is not particularly striking. Use of $Bu_4N^+Br^-$ as the phase-transfer agent increases the amount of **10** coproduced (run 13). When CO is omitted from the reaction, the carbonylation becomes approximately stoichiometric in iron (run 14). Runs 15–17 illustrate the use of butyl halides as substrates; when the substrate is sufficiently reactive, ketonic byproduct formation occurs very readily.

The ketone **10** is certainly an unusual and unexpected byproduct, and it formally appears to be the product of

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Table I. $Fe(CO)_5$-Catalyzed Esterification of Alkyl and Aralkyl Halides by CO and Alcohols

	reactants				products				
run	RX (g)	solvent (mL)	others (g)	condns[a]	ester (g)	ester, %	other (g)	other, %	iron turnovers
1	$PhCH_2Br$ (6.0)	MeOH (60)	K_2CO_3 (5.8)	a	$PhCH_2CO_2CH_3$ (3.6)	68	$PhCH_2OCH_3$ (0.2)	5	9.5
2	$PhCH_2Br$ (6.0)	MeOH (55)	K_2CO_3 (5.8)	b	$PhCH_2CO_2CH_3$ (2.8)	52	$PhCH_2OCH_3$ (0.8)	19	6.3
3	$PhCH_2Br$ (6.0)	MeOH (30) THF (25)	K_2CO_3 (5.8)	b	$PhCH_2CO_2CH_3$ (2.3)	43	$PhCH_2OCH_3$ (0.7)	16	5.2
4	$PhCH_2Br$ (6.0)	MeOH (30) *N*-methyl-2-pyrrolidone (25)	K_2CO_3 (5.1)	b	$PhCH_2CO_2CH_3$ (1.9)	34	$PhCH_2OCH_3$ (1.3)	31	4.1
5	$PhCH_2Br$ (6.0)	MeOH (30) CH_3CN (25)	K_2CO_3 (5.8)	b	$PhCH_2CO_2CH_3$ (1.7)	32	$PhCH_2OCH_3$ (2.4)	38	3.9
6	$PhCH_2Cl$ (16.4)	MeOH (200)	K_2CO_3 (15.2) KI (18.3)	c	$PhCH_2CO_2CH_3$ (9.8)	65	None	0	8.7
7	C_4H_9I (17.9)	MeOH (200)	K_2CO_3 (15.2) KI (18.3)	d	$C_4H_9CO_2CH_3$ (7.5)	65	$C_4H_9OCH_3$ (trace)		8.7
8	$PhCH_2Br$ (11.5)	EtOH (100)	K_2CO_3 (11.2)	a	$PhCH_2CO_2C_2H_5$ (6.9)	45			6.7
9	$PhCH_2Br$ (15.8)	MeOH (420)	K_2CO_3 (14.1)	e	$PhCH_2CO_2CH_3$ (2.0)	22	$PhCH_2OCH_3$ (1.9)	17	9.4
10	$PhCH_2Br$ (15.8)	MeOH (420)	K_2CO_3 (14.1)	f	$PhCH_2CO_2CH_3$ (2.8)	29	$PhCH_2OCH_3$ (1.9)	17	12.9
11	$PhCH_2Br$ (15.8)	MeOH (420)	K_2CO_3 (14.1)	g	$PhCH_2CO_2CH_3$ (3.6)	38	$PhCH_2OCH_3$ (1.7)	15	16.3

[a] Conditions: (a) 1 atm CO, 0.4 mL $Fe(CO)_5$, room temperature, overnight. (b) 1 atm CO, 0.4 mL $Fe(CO)_5$, room temperature, 2 h. (c) 1 atm CO, 1.0 mL $Fe(CO)_5$, room temperature, 24 h. (d) 1 atm CO, 1.0 mL $Fe(CO)_5$, room temperature, 5 days. (e) 30 psig CO, 0.2 mL $Fe(CO)_5$, room temperature, 12 h. (f) 300 psig CO, 0.2 mL $Fe(CO)_5$, room temperature, 12 h. (g) 1000 psig CO, 0.2 mL $Fe(CO)_5$, room temperature, 12 h.

Table II. $Fe(CO)_5$-Catalyzed Acid Synthesis under Phase-Transfer Conditions

run	RX (g)	cosolvent (mL)	phase-transfer agent (g)	time	condns[a]	product (g)	product, %	iron turnovers
1	$PhCH_2Cl$ (38.5)	none	$PhCH_2(C_2H_5)_3NCl$ (1.7)	2 days	a	$PhCH_2CO_2H$ (6.1)	15	6
2	$PhCH_2Cl$ (38.5)	none	$PhCH_2(C_2H_5)_3NCl$ (1.7)	4 h	b	$PhCH_2CO_2H$ (2.7)	7	2.8
3	$PhCH_2Br$ (51.8)	none	$PhCH_2(C_2H_5)_3NCl$ (1.7)	1 week	a	$PhCH_2CO_2H$ (4.4) $[PhCH_2CHPh]_2CO$ (1.8)	11 6	4.2 0.6
4	$PhCH_2Cl$ (38.5)	hexane (50)	$PhCH_2(C_2H_5)_3NCl$ (1.7)	2 days	a	$PhCH_2CO_2H$ (8.3) $[PhCH_2]_2CO$ (trace)	20	8.1
5	$PhCH_2Cl$ (38.5)	hexane (50)	$PhCH_2(C_2H_5)_3NCl$ (8.5)	2 days	a	$PhCH_2CO_2H$ (12.7) $[PhCH_2CHPh]_2CO$ (trace) $[PhCH_2]_2CO$ (trace)	31	12.4
6	$PhCH_2Cl$ (38.5)	$PhCH_3$ (50)	$PhCH_2(C_2H_5)_3NCl$ (8.5)	2 days	a	$PhCH_2CO_2H$ (13)	32	12.8
7	$PhCH_2Cl$ (38.5)	CH_2Cl_2 (50)	$PhCH_2(C_2H_5)_3NCl$ (1.7)	1 day	a	$PhCH_2CO_2H$ (1.8)	4	1.6
8	$PhCH_2Cl$ (38.5)	none	$PhCH_2(C_2H_5)_3NCl$ (1.7)	12 h	c	$[PhCH_2CHPh]_2CO$ (5.0)	17	1.7
9	$PhCH_2Cl$ (38.5)	none	$PhCH_2(C_2H_5)_3NCl$ (1.7)	1 day	d	$PhCH_2CO_2H$ (3.2)	8	3.2
10	$PhCH_2Cl$ (38.5)	none	$PhCH_2(C_2H_5)_3NCl$ (1.7)	3 days	e	$PhCH_2CO_2H$ (5.0)	12	4.9 (Fe_2 units)
11	$PhCH_2Cl$ (38.5)	none	$PhCH_2(C_2H_5)_3NCl$ (1.7)	5 days	f	$PhCH_2CO_2H$ (10.7)	26	10.5 (Fe_3 units)
12	$PhCH_2Cl$ (38.5)	none	$PhCH_2(C_2H_5)_3NCl$ (1.7)	12 h	g	$PhCH_2CO_2H$ (8.3)	20	8.8
13	$PhCH_2Cl$ (38.5)	none	$[n\text{-}C_4H_9]_4NBr$ (2.4)	2 days	a	$PhCH_2CO_2H$ (7.8) $[PhCH_2CHPh]_2CO$ (4.1)	19 13	7.6 1.3
14	$PhCH_2Cl$ (38.5)	hexane (50)	$PhCH_2(C_2H_5)_3NCl$ (1.7)	1 day	h	$PhCH_2CO_2H$ (1.4)	3	1.2
15	$n\text{-}C_4H_9Cl$ (28.0)	none	$PhCH_2(C_2H_5)_3NCl$ (1.7)	1 day	a	none	0	
16	$n\text{-}C_4H_9Br$ (41.1)	none	$PhCH_2(C_2H_5)_3NCl$ (1.7)	2 days	a	$n\text{-}C_4H_9CO_2H$ (0.2)	0.7	0.3
17	$n\text{-}C_4H_9I$ (55.2)	none	$PhCH_2(C_2H_5)_3NCl$ (1.7)	3 days	a	$n\text{-}C_4H_9CO_2H$ (1.4) $[n\text{-}C_4H_9]_2CO$ (2.9)	5 13	2 2.7

[a] Conditions: (a) 1.0 mL of $Fe(CO)_5$, 200 mL of H_2O, 36 g of NaOH, 1 atm of CO, room temperature. (b) 1.0 mL of $Fe(CO)_5$, 200 mL of H_2O, 36 g of NaOH, 1 atm of CO, 55-70 °C. (c) 1.0 mL of $Fe(CO)_5$, 36 mL of H_2O, 36 g of NaOH, 1 atm CO, room temperature. (d) 1.0 mL of $Fe(CO)_5$, 800 mL of H_2O, 36 g of NaOH, 1 atm of CO, room temperature. (e) 2.7 g of $Fe_2(CO)_9$, 200 mL of H_2O, 36 g of NaOH, 1 atm of CO, room temperature. (f) 3.8 g of $Fe_3(CO)_{12}$, 200 mL of H_2O, 36 g of NaOH, 1 atm of CO, room temperature. (g) 1.0 mL of $Fe(CO)_5$, 200 mL of H_2O, 36 g of NaOH, 1500 psi CO, room temperature. (h) 1.0 mL of $Fe(CO)_5$, 200 mL of H_2O, 36 g of NaOH, no CO, room temperature.

alkylation of dibenzyl ketone with 2 mol of benzyl halide. The analytical and spectral data support the proposed structure (see Experimental Section). The NMR spectrum confirms the presence of asymmetric centers in the molecule, and the benzylic protons appear as three distinct resonances at δ 2.74, 3.26, and 3.86. The two high-field protons ($PhCH_aH_b$) have a geminal coupling constant of 15 Hz and are coupled to the methine proton by 8 and 10 Hz. The methine proton at δ 3.86 appears as an overlapping doublet of doublets (J = 8 and 10 Hz). An infrared absorption at 1715 cm^{-1} supports the presence of the ketone functionality. The parent ion at m/e 390 is consistent with the formulation $C_{29}H_{26}O$, and the base peak at m/e 181 corresponds to the $C_{14}H_{13}$ fragment. A related polyalkylation occurs in the cobalt carbonyl catalyzed carbonylation of aryl halides under phase-transfer conditions.[17]

The mechanistic details of the phase-transfer reaction have not been elucidated. Presumably the anions $HFe(CO)_4^-$ or $Fe(CO)_4^{2-}$ could be generated during the reaction. Kimura and co-workers investigated a phase-transfer-catalyzed reaction where alkyl halides were stoichiometrically converted to ketones in the presence of $Fe(CO)_5$, water, NaOH, tetrabutylammonium bromide, and benzene:[18]

$$RX \xrightarrow[Bu_4N^+Br^-,\ H_2O]{Fe(CO)_5,\ NaOH} RC(O)R$$

They found that the reaction produces a maximum of 2 mol of ketone per mol of $Fe(CO)_5$. This is in accord with our findings in the catalytic system where the ketone byproduct formation appears to remove the active iron from the catalytic system. Kimura et al. proposed that $Fe(CO)_4^{2-}$ is the active species in the ketone formation and that $HFe(CO)_4^-$ is the active species in hydrocarbon formation. Alper and des Abbayes[7] studied a similar catalytic carbonylation of benzyl bromide to phenylacetic acid in a phase-transfer system with $Co_2(CO)_8$ as the catalyst and NaOH as the base. They proposed that $Co(CO)_4^-$ was the active catalyst in that system. Related carbonylations have been effected by $Ni(CO)_4$ in the presence of base.[19]

A recent publication by des Abbayes and co-workers describes a phase-transfer system very similar to the one described herein.[20] These workers have also discovered that under the proper conditions, benzyl halides can be carbonylated to arylacetic acids under phase-transfer conditions by using catalytic amounts of $Fe(CO)_5$ an 1 atm of CO at room temperature. The dianion $Fe(CO)_4^{2-}$ is proposed by des Abbayes to be the species that initiates the catalysis.

Experimental Section

Melting points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 283B spectrometer. Routine ^1H NMR spectra were recorded on a Varian EM-360 spectrometer, and 100-MHz spectra were recorded on a JEOL JNM-MH-100 spectrometer and were performed in $CDCl_3$ with Me_4Si as an internal standard. Mass spectral analyses were performed on a Vacuum Generators ZAB-2F spectrometer. Reagent-grade materials were used in all synthese without further purification.

Typical Methyl Phenylacetate Synthesis. K_2CO_3 (5.8 g, 42 mmol) and methanol (50 mL) were charged into a 100-mL, three-necked flask fitted with a three-way gas inlet, magnetic stirring bar, rubber septum, and a glass stopper. The flask was purged with CO and maintained at positive CO pressure during the reaction by means of a rubber bladder attached to the gas inlet. $Fe(CO)_5$ (0.40 mL, 2.5 mmol) was added by means of a syringe. The reaction was stirred 15 min, and then a mixture of benzyl bromide (6.0 g, 35 mmol), mesitylene (2.0 mL), and methanol (10 mL) was added; the reaction mixture was stirred at room temperature overnight. The reaction mixture was poured into a mixture of 1% hydrochloric acid (70 mL) and diethyl ether (70 mL). The etherial phase was washed a second time with 1% hydrochloric acid (50 mL) followed by an aqueous sodium bicarbonate wash, dried over $MgSO_4$, filtered, and concentrated under vacuum to yield a liquid product (3.81 g), which by NMR analysis consisted of methyl phenylacetate (3.6 g, 24 mmol, 68% yield) and methyl phenyl ether (0.21 g, 1.7 mmol, 5% yield). This represents 9.5 turnovers in iron.

Typical Phenylacetic Acid Synthesis under Phase-Transfer Conditions. NaOH (36 g, 0.9 mol), water (200 mL), benzyltriethylammonium chloride (8.5 g, 0.0375 mol), hexane (50 mL), and benzyl chloride (35 mL, 0.3 mol) were charged into a 500-mL three-necked flask containing a magnetic stirring bar and fitted with a gas bladder, a septum, and a CO gas inlet. The stirred mixture was purged with nitrogen and then with CO. Iron pentacarbonyl (1.0 mL, 0.0075 mol) was injected, and the gas bladder was filled with CO. The mixture was stirred for 2 days at room temperature, and the bladder was reinflated with CO as it was depleted. The mixture was acidified with concentrated aqueous HCl and then extracted with CH_2Cl_2 (2 × 100 mL). Iodine (0.75 g) was added to the CH_2Cl_2 phase, which was then stirred for 1 h. This solution was stirred for an additional hour with 5% aqueous sodium thiosulfate (100 mL). The dichloromethane phase was back-washed with 5% aqueous NaOH (3 × 100 mL) that was then acidified with concentrated HCl and reextracted with CH_2Cl_2 (3 × 100 mL). This solution was dried ($MgSO_4$), filtered, and concentrated under vacuum to yield phenylacetic acid (12.7 g, 31%).

Characterization of Ketone 10. The acid synthesis was performed under the conditions described in run 3, Table II. After CO uptake had stopped, concentrated HCl (60 mL) was added and the entire mixture was extracted with diethyl ether (3 × 100 mL). The etherial phase was extracted with 5% aqueous NaOH (3 × 100 mL) to remove acidic products and then with water (100 mL). The etherial phase was dried ($MgSO_4$), filtered, and concentrated under vacuum to yield an oil containing suspended white solids. Ethanol was added, and the mixture was filtered. The solids (1.8 g) were washed further with ethanol, recrystallized from ethanol, and dried at 56 °C (0.2 mmHg) for 8 h to yield an analytical sample (1.2 g, mp 119.0–119.5 °C): IR (CH_2Cl_2) 1715 cm^{-1}; NMR δ 2.74 (dd, 2 H, J = 15 Hz, J = 8 Hz), 3.26 (dd, 2 H, J = 15 Hz, J = 10 Hz), 3.86 (overlapping dd, 2 H, J = 8 Hz, J = 10 Hz), 6.59–7.40 (m, 20 H); mass spectrum, parent ion m/e 390, base peak at m/e 181.

Anal. Calcd for $C_{29}H_{26}O$: C, 89.19; H, 6.71. Found: C, 89.24; H, 6.77.

Registry No. $PhCH_2Br$, 100-39-0; $PhCH_2Cl$, 100-44-7; C_4H_9I, 542-69-8; n-C_4H_9Br, 109-65-9; n-C_4H_9Cl, 109-69-3; $Fe(CO)_5$, 13463-40-6; $PhCH_2CO_2CH_3$, 101-41-7; $C_4H_9CO_2CH_3$, 624-24-8; $PhCH_2CO_2H$, 103-82-2; n-$C_4H_9CO_2H$, 109-52-4; $[n\text{-}C_4H_9]_2CO$, 502-56-7; $[PhCH_2CHPh]_2CO$, 89322-22-5; $PhCH_2(C_2H_5)_3NCl$, 56-37-1; $[n\text{-}C_4H_9]_4NBr$, 1643-19-2.

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