

## Phase Transfer Generation of Acyltetracarbonyliron Anions: their Role in the Phase Transfer Carbonylation of Reactive Halides to give Carboxylic Acids and Symmetrical and Unsymmetrical Ketones

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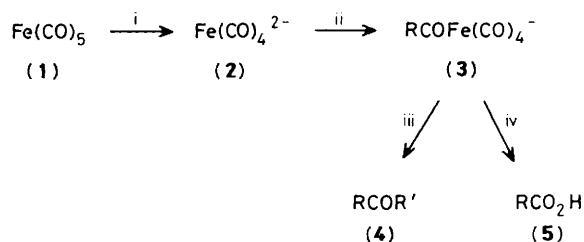
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Acyltetracarbonyliron anions  $\text{RCOFe}(\text{CO})_4^-$  (**3**) are readily synthesised under mild phase transfer (PT) conditions from pentacarbonyliron and reactive organic halides; the *in situ* generated anions (**3**) ( $\text{R} = \text{ArCH}_2$ ) are the true catalysts in the PT carbonylation of benzyl halides to give ketones or carboxylic acids.

The reactions shown in Scheme 1, although stoichiometric and needing a dry medium, have proved to be very useful for the carbonylation of organic halides to give ketones or acids.<sup>1</sup> We reported recently that pentacarbonyliron (**1**), introduced into a liquid-liquid phase transfer (PT) system, could induce the carbonylation of benzyl halides to give carboxylic acids (**5**) or ketones (**4**;  $\text{R} = \text{R}' = \text{ArCH}_2$ ) under very mild conditions (Scheme 2). We now report that acyltetracarbonyliron anions (**3**) are readily generated under suitable PT conditions and are the true catalysts of the PT carbonylation reactions in Scheme 2.

The following reagents were introduced into an autoclave at  $+10^\circ\text{C}$  under a CO atmosphere: 10 ml  $\text{H}_2\text{O}$ , 10 ml  $\text{CH}_2\text{Cl}_2$ , 10 mmol NaOH, 2 mmol  $\text{Bu}_4\text{N}^+\text{HSO}_4^-$ , 1.5 mmol halide (**6**) (see Table 1), 1.5 mmol  $\text{Fe}(\text{CO})_5$  (**1**). The CO pressure was then raised to 10 atm, and magnetic stirring fixed at 1200 r.p.m. for one night, during which halide (**6**) completely disappeared

(g.c. or t.l.c.). The i.r. spectrum of the organic layer was fully consistent with that reported for anion (**3**), with benzyl chloride as the starting halide (**6**;  $\text{R} = \text{PhCH}_2$ ).<sup>3</sup> Very similar results were observed for other halides (Table 1). Under these

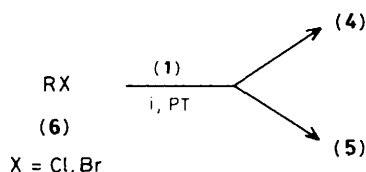
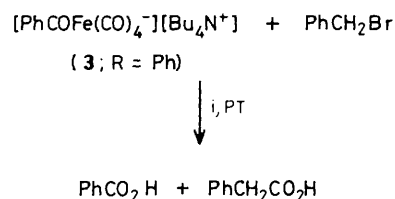
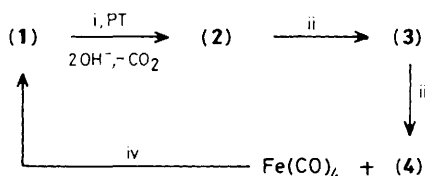
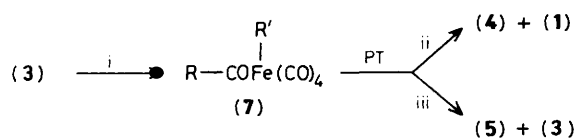


**Scheme 1.** i, Reduction, dry medium; ii, RX, CO; iii, R'X; iv, oxidation (RX, R'X = alkyl, aryl halides).

**Table 1.** Phase transfer synthesis of the acyltetracarbonyliron anions (3) and ketones (4) from halides RCl (6) (see Scheme 3; RX = RCl, R'X = MeI).

R		PhCH <sub>2</sub>	N≡C-CH <sub>2</sub>	PhCH=CH-CH <sub>2</sub> <sup>a</sup>	Bu <sup>c</sup> OCOCH <sub>2</sub>
I.r. data for RCOFe(CO) <sub>4</sub> <sup>-</sup> (3)	$\left\{ \begin{array}{l} \nu_{\text{C}=\text{O}} \\ \nu_{\text{C}=\text{O}} \\ \text{Others} \end{array} \right.$	2015 m <sup>b</sup>	2015 m	1995 m	2005 m
		1915 sh	1910 sh	1910 sh	1895 vs
		1890 vs	1890 vs	1880 vs	
		1610 m	1620 m	1615 w	1570 w
			2195 m ( $\nu_{\text{C}=\text{N}}$ )	1590 w ( $\nu_{\text{C}=\text{C}}$ )	1660 m ( $\nu_{\text{C}=\text{O}}$ ester)
% Yield of RCOMe (4) <sup>c</sup>		75	65	64	83

<sup>a</sup> Reaction at 0°C. <sup>b</sup> Fully consistent with ref. 3. <sup>c</sup> <sup>1</sup>H N.m.r., i.r., and mass spectra are fully consistent with the proposed formulae. Yields for isolated ketones (4) by t.l.c.

**Scheme 2.** i, H<sub>2</sub>O, Bu<sub>4</sub>N<sup>+</sup>OH<sup>-</sup>, CH<sub>2</sub>Cl<sub>2</sub>, CO, 1200 r.p.m. R = R' = ArCH<sub>2</sub>.**Scheme 5.** i, H<sub>2</sub>O, 1 M NaOH, (Bu<sub>4</sub>N<sup>+</sup>)<sub>2</sub>SO<sub>4</sub><sup>2-</sup>, CH<sub>2</sub>Cl<sub>2</sub>, CO (40 atm), +10°C, 1200 r.p.m.**Scheme 3.** i, H<sub>2</sub>O, Bu<sub>4</sub>N<sup>+</sup>HSO<sub>4</sub><sup>-</sup>, NaOH, CH<sub>2</sub>Cl<sub>2</sub>, CO atmosphere, +10°C, 1200 r.p.m.; ii, RX, CO (10 atm); iii, R'X; iv, CO. R = R' = ArCH<sub>2</sub>. For R ≠ R', see Table 1.**Scheme 4.** i, R'X, CO; PT system as in Scheme 3; ii, CO; iii, OH<sup>-</sup>, CO. R = R' = PhCH<sub>2</sub>.

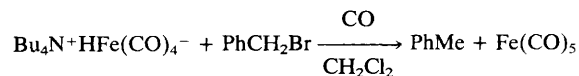
conditions, anions (3) (maintained in the organic phase as tetrabutylammonium salts) did not react with the introduced halide (6). Further methylation (as in Scheme 1, iii; R'X = MeI) after stirring was stopped, gave ketones (4) and pentacarbonyliron (1) in high yields (65 to 85%, Table 1). Thus, PT reactions proceed *via* the same steps as in Scheme 1, when conducted in a dry medium: the transient generation of the very reactive dianion (2) under mild PT conditions has been previously established;<sup>4</sup> further rapid trapping with a reactive halide gives the anion (3). Furthermore, from our observation that pentacarbonyliron is regenerated by alkylation of anion (3) under a carbon monoxide atmosphere, we

must deduce that the PT reaction giving ketones (4) in Scheme 2 is a catalytic process (see Scheme 3).

This catalytic cycle for several other catalytic reactions, showed (by i.r. spectroscopy) the presence of anion (3) (R = PhCH<sub>2</sub>, Table 1) in 100% yield from (1) [determined by reaction with MeI and g.c. analysis of the resulting ketone (4; R = PhCH<sub>2</sub>, R' = Me)]. We therefore suspected that products (4) and (5) in Scheme 2 proceeded through the same intermediate (7) (Scheme 4) from which the two competing reactions giving (4) or (5) occur.

In agreement with the well known thermal instability of complexes such as (7),<sup>‡</sup> the ketone : acid ratio increased from

<sup>‡</sup> The same results were obtained by using Bu<sub>4</sub>N<sup>+</sup>HFe(CO)<sub>4</sub><sup>-</sup> instead of Fe(CO)<sub>5</sub>. However, it should not be deduced that this salt is the catalyst in the PT reactions in Scheme 2. We showed, in separate experiments, that it rapidly reacts with benzyl bromide according to reaction (1) to give quantitatively toluene and pentacarbonyliron, from which the true catalyst (3) could be generated *in situ*. For a discussion against the PT generation of the HFe(CO)<sub>4</sub><sup>-</sup> anion, see ref. 4.



<sup>‡</sup> The closely related neutral tetracarbonylferracyclopentane CH<sub>2</sub>[CH<sub>2</sub>]<sub>3</sub>Fe(CO)<sub>4</sub> was characterized recently. It shows a high thermal instability, and gives cyclopentanone by heating at +20°C under an atmosphere of carbon monoxide (ref. 5).

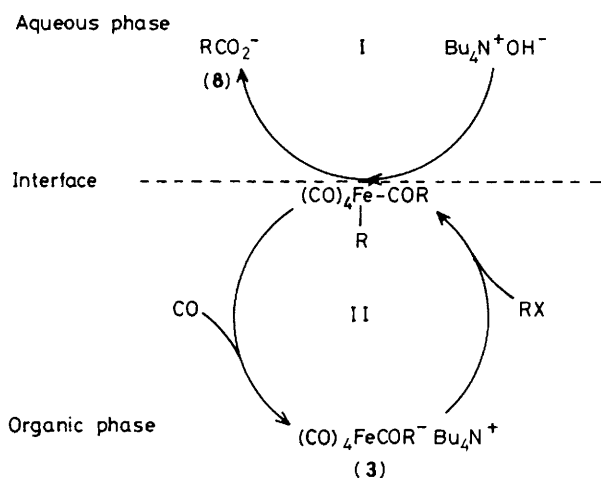


Figure 1

0.16:1 at 20°C to 0.7:1 at 30°C [85% overall yield of (4) + (5)] in Scheme 2. The crossover experiment shown in Scheme 5 was also consistent with the base-catalysed cleavage of (7). In the absence of  $\text{PhCH}_2\text{Br}$ , anion (3;  $\text{R}=\text{Ph}$ ) was found to be very stable in the PT system of Scheme 5, and no production of benzoic acid could be detected. On introducing  $\text{PhCH}_2\text{Br}$  [10:1  $\text{PhCH}_2\text{Br}$ : (3)], a mixture of both acids  $\text{PhCO}_2\text{H}$  [40% yield from (3)] and  $\text{PhCH}_2\text{CO}_2\text{H}$  (80% yield from  $\text{PhCH}_2\text{Br}$ ) was obtained after 4 h.

Figure 1 shows the catalytic cycle for the carbonylation of benzyl halides to give carboxylic acids in liquid-liquid PT systems. Particularly noteworthy are the following points. (i) Since the hydroxide anion is not extractable into the organic phase in these conditions, cleavage I occurs at the liquid-liquid interface: consequently, the ketone: acid ratio (4):(5) of the two competing reactions (Scheme 4) is completely upset by lowering the stirring speed: 0.16:1 at 1200 r.p.m., and 1.46:1 at 800 r.p.m. [85% overall yield of (4) + (5)]. (ii) The catalyst (3) remains in the organic phase, and the ionised product (8) is expelled into the aqueous phase, securing a very simple separation. §

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### References

- 1 J. P. Collman, *Acc. Chem. Res.*, 1975, **8**, 342.
- 2 G. Tanguy, B. Weinberger, and H. des Abbayes, *Tetrahedron Lett.*, 1983, **24**, 4005; 1984, **25**, 5529.
- 3 W. O. Siegl and J. P. Collman, *J. Am. Chem. Soc.*, 1972, **94**, 2516.
- 4 B. Weinberger, G. Tanguy, and H. des Abbayes, *J. Organomet. Chem.*, 1985, **280**, C31.
- 5 E. Lindner, E. Schauss, W. Hiller, and R. Fawzi, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 711.
- 6 H. des Abbayes, A. Buloup, and G. Tanguy, *Organometallics*, 1983, **2**, 1730.

§ The PT catalytic system described in Figure 1 for anion (3) presents a close analogy to that described for the tetracarbonylcobalt anion with respect to the marked effect of stirring, and catalyst-product separation (ref. 6).