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Journal of Organometallic Chemistry 486 (1995) 275–277

Journal of Organo metallic Chemistry

Preliminary communication

Synthesis of benzophenone by carbonylation of iodobenzene with $[Bu^n_4N][HFe(CO)_4]$

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Received 19 may 1994

Abstract

The reaction of $[HFe(CO)_4]^-$ with iodobenzene under phase-transfer conditions (aq. NaOH/benzene, Bu^n_4NBr) for 24 h at 70°C under carbon monoxide at one atmosphere affords benzophenone in 85% yield.

Keywords: Pentacarbonyliron; Carbonylation; Aryl iodides; Synthesis; Benzophenone

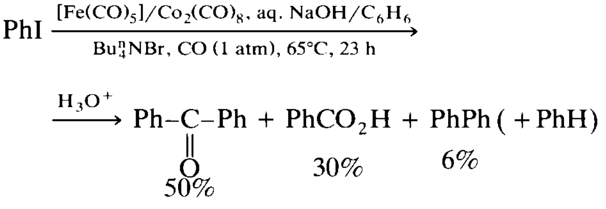
It is well established that $Na_2[Fe(CO)_4]$ is a supernucleophile that reacts with primary alkyl halides or tosylates by an S_N2 process to afford alkyliron complexes $Na[RFe(CO)_4]$ [1–3]. Under the action of an added donor L (CO or PPh_3), a carbonyl ligand of the ferrate complex undergoes migratory insertion, giving the acyliron complexes $Na[R(CO)Fe(CO)_3L]$. These complexes are synthetically useful, since they can be used as acyl anion equivalents; for example for the formation of carbon–carbon bonds by reaction with reactive alkylating agents (ketone synthesis) [1–3].

It is also well known that $Na_2[Fe(CO)_4]$ does not react with iodoarenes, at least under the conditions used for its reaction with alkyl iodides (NMP–THF solvent mixture) [1,4]. Furthermore, literature data indicate that acyliron complexes do not react with aryl iodides. The latter reaction only occurs in the presence of a $Pd(PPh)_3$-$ZnCl_2$ catalytic system [5].

As part of our interest in developing new applications of the hydridotetracarbonylferrates $M[HFeCO)_4]$ [6], we have reported that these complexes do react with aryl iodides in a catalytic manner to afford the corresponding reduction products ArH (Eq. (1)) [7].

$$ArI \xrightarrow[\text{CO (1 atm), 60°C}]{[Fe(CO)_5](cat)/K_2CO_3/MeOH} ArH \qquad (1)$$

The mechanism of this reaction has been proposed to involve an electron transfer from $[HFe(CO)_4]^-$ to the aryl iodide [8], a process similar to the initiation step of $S_{RN}1$ substitution reactions of aryl halides with nucleophiles. This feature is the basis for the cobalt carbonyl-catalyzed carbonylation of iodobenzene to benzoic acid by using a bimetallic $[HFe(CO)_4]^-$/$[Co(CO)_4]^-$ system in which the carbonylcobaltate plays the role of nucleophile, intercepting the phenyl radicals [8,9]. More interestingly, it was found that, under slightly different conditions this bimetallic system afforded benzophenone as the major product (50% yield) (Eq. (2)) [10]. This catalytic, direct carbonylative coupling of aryl halides to the corresponding symmetrical benzophenones is unprecedented. The mechanism of this reaction, however, is still obscure.



$$PhI \xrightarrow[\text{Bu}^n_4\text{NBr, CO (1 atm), 65°C, 23 h}]{[Fe(CO)_5]/Co_2(CO)_8,\ \text{aq. NaOH}/C_6H_6} \xrightarrow{H_3O^+} \underset{50\%}{Ph\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}Ph} + \underset{30\%}{PhCO_2H} + \underset{6\%}{PhPh} (+PhH) \qquad (2)$$

$PhI/[Fe(CO)_5]/[Co_2(CO)_8] = 20/1.8/0.5$
Conversion: 95%
$H_2O/C_6H_6 = 50/30$ ml

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SSDI 0022-328X(94)05112-7

Table 1
Influence of the water/benzene ratio

Run	% H_2O (vol)	% C_6H_6 (vol)	PhI conv. (%) [a]	Ph(CO)Ph (%) [a]	$PhCO_2H$ (%) [b]	Ph–Ph (%) [a]	Selectivity % [c]
1	25	75	20	5	5	4	25
2	37.5	62.5	38	12	14	6	31
3	50	50	38	15	9	4	40
4	62.5	27.5	48	22	13	6	46
5	75	25	51	28	15	2	55
6	87.5	12.5	84	55	7	4	66

Total solvent volume is 80 ml.
$[Fe(CO)_5]$ = 1.8 mmol; PhI = 20 mmol; NaOH = 8 M/l; Bu^n_4NBr = 3 mmol; 70°C; 750 rev min^{-1}; 24 h.
[a] Determined by GC analysis with dodecane as internal standard (OV_1 capillary column); [b] isolated yield; [c] Ph(CO)Ph %/PhI conversion %.

Control experiments aimed at demonstrating the synergy between the two carbonylmetallates for the above reaction were conclusive [10]. However, they indicated that, in the absence of the carbonylcobaltate, $[HFe(CO)_4]^-$ slowly reacts with iodobenzene to afford a mixture of benzoic acid and benzophenone in low yield, along with the expected reduction products (biphenyl and probably benzene) (vide infra, run 4, Table 1). We were thus interested to examine in more detail this unexpected reactivity of $[HFe(CO)_4]^-$ giving benzophenone. We have now found conditions under which the reaction of $[HFe(CO)_4]^-$ with iodobenzene affords benzophenone in high yield.

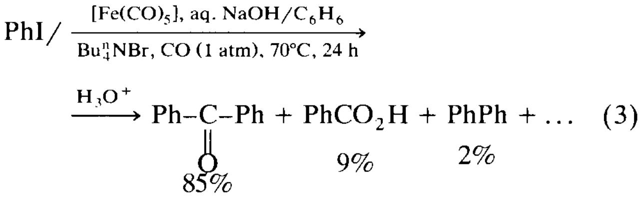
A brief study of the influence of some reaction parameters highlighted the determining influence of two of them on both the reaction rate and the selectivity for benzophenone vs. benzoic acid and reduction products. The first parameter is the solvent ratio (Table 1).

The highest selectivity for benzophenone is obtained (run 6) with the highest water/benzene ratio (with still higher ratios, the reaction results were inconsistent). Under the above conditions (run 6), the reaction is catalytic (6.9 mmol of carbonylation products formed using 1.8 mmol $[Fe(CO)_5]$).

The second important parameter is the concentration of the aqueous sodium hydroxide. This study was carried out with a $[Fe(CO)_5]$/PhI ratio of 2.9/10 (mmol) to ensure a total conversion within 24 h (Table 2).

The best results are obtained with an 8 M aqueous sodium hydroxide solution (run 9). Using less concentrated NaOH solutions results in a decreased carbonylation yield (with probably an increase in benzene formation) whereas with higher NaOH concentrations agitation of the reaction medium (750 rev min^{-1}) is poorly efficient.

Taking the results of Tables 1 and 2 together provides the reaction conditions for obtaining a nearly quantitative overall carbonylation yield (94%) and a high selectivity for benzophenone (85%, Eq. (3)).



$$\mathrm{PhI}/\xrightarrow[\mathrm{Bu^n_4NBr,\ CO\ (1\ atm),\ 70^\circ C,\ 24\ h}]{\mathrm{[Fe(CO)_5],\ aq.\ NaOH/C_6H_6}} \xrightarrow{H_3O^+} \underset{85\%}{\mathrm{Ph{-}\underset{\underset{O}{\|}}{C}{-}Ph}} + \underset{9\%}{\mathrm{PhCO_2H}} + \underset{2\%}{\mathrm{PhPh}} + \ldots \quad (3)$$

$PhI[Fe(CO)_5] = 10/2.9$
Conversion 100%
$H_2O/C_6H_6 = 70/10$ ml

The use of carbonylferrates under the mild conditions described above is easy and inexpensive. This new reaction enhances the synthetic utility of carbonylferrates which, up to now, have been considered inefficient for the carbonylative coupling of aryl halides. Work is in progress to determine the scope and limitations of this reaction and to gather further information with the hope of clarifying the reaction mechanism.

Table 2
Influence of the concentration of the sodium hydroxide solution

Run	aq. NaOH (mol/l^{-1})	PhI conv. (%) [a]	Ph(CO)Ph (%) [a]	$PhCO_2H$ (%) [b]	Ph–Ph (%) [a]	PhH (%) [c]	Selectivity (%) [d]
7	2	100	50	16	2	32	50
8	4	100	62	14	2	22	62
9	8	100	72	18	2	8	72

$[Fe(CO)_5]$ = 2.9 mmol; PhI = 10 mmol; H_2O = 60 ml; C_6H_6 = 20 ml; Bu^n_4NBr = 3 mmol; 70°C; 750 rev min^{-1} 24 h.
[a] Determined by GC analysis with dodecane as internal standard (OV_1 capillary column); [b] isolated yield; [c] calculated by difference, [d] Ph(CO)Ph %/PhI conversion %.

Acknowledgment

The authors wish to thank Drs. R. Chauvin, L. Rosenberg and D. Neibecker for fruitful discussions. Special thanks are due to Dr. L. Rosenberg for her help in editing the English of this manuscript.

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