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Bimetallic catalysis: synthesis of benzophenones through carbonylation of aryl iodides catalysed by $Fe(CO)_5$–$Co_2(CO)_8$ systems.

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Abstract

The direct, catalytic carbonylation of aryl iodides to give the corresponding benzophenones is reported for the first time. Under phase transfer conditions (aq. $NaOH/C_6H_6/Bu_4NBr$) and under 1 atm pressure of carbon monoxide, iron pentacarbonyl alone promotes the conversion of iodobenzene to benzophenone and benzoic acid, whereas dicobaltoctacarbonyl alone promotes a slow carbonylation to give solely benzoic acid. A synergetic effect is observed when the reaction is carried out in the presence of catalytic amounts of both carbonyl metals, and benzophenone can be isolated in more than 50% yield. Under these conditions, *o*-iodotoluene affords the corresponding 2,2′-dimethylbenzophenone in 47% isolated yield.

Introduction

The carbonylation of aryl halides to give aromatic acids and their derivatives is catalyzed by transition metal salts or complexes as catalyst precursors [1,2]. Although these reactions were first carried out under drastic conditions, several methods have now been reported in which the transformations can be performed under atmospheric (or low) carbon monoxide pressure and at temperatures below 100 °C [3–6].

The carbonylation of aryl halides to give the corresponding diaryl ketones ArC(O)Ar is much less well known. Benzophenone has been reported to be formed in the reaction of iodobenzene with either $Fe_3(CO)_{12}$ [7] or $Ni(CO)_4$ [8]. The reaction of iodobenzene with $Co_2(CO)_8$, followed by oxidation with iodine, is also known to give benzophenone [9]. The related carbonylation of arylmercuric salts ArHgX to give ArC(O)Ar can be brought about by transition metal carbonyl complexes such as $Co_2(CO)_8$ [10] or $Ni(CO)_4$ [11]. However, the above reactions involve stoichiometric amounts of metalcarbonyls. The transition metal (Pd or Rh)

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catalyzed synthesis of diaryl ketones is also known, but always involves prior conversion of the aryl halide, for example into arylmercuric [12,13] or diaryliodonium salts [14].

As part of our study aimed at developing the use of $KHFe(CO)_4$ in organic synthesis and catalysis [15–19], we have recently presented a preliminary report about the reactions of this complex with aryl halides in methanol [15]. It was found that $KHFe(CO)_4$ can bring about the selective reduction of aryl iodides to the corresponding arenes. More interestingly, it was also found that, in the presence of an excess of base, the reactions are catalytic under atmospheric carbon monoxide pressure (eq. 1).

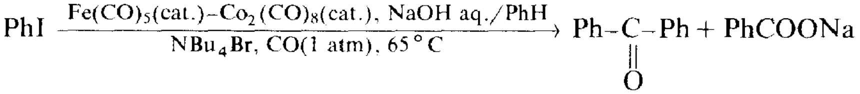
$$\mathrm{ArI} \xrightarrow[\mathrm{MeOH,\ 60\,^\circ C}]{\mathrm{Fe(CO)_5(cat.)/K_2CO_3,\ CO(1\ atm)}} \mathrm{ArH} \qquad (1)$$

Mechanistic considerations and further investigations led us to the finding that the carbonylation of iodobenzene to benzoic acid can be catalyzed, under very mild conditions, by a bimetallic system based on $Fe(CO)_5$ and $Co_2(CO)_8$ under somewhat unusual phase transfer conditions (eq. 2) [16].

$$\mathrm{PhI} \xrightarrow[\mathrm{NBu_4Br,\ CO(1\ atm),\ 60\,^\circ C}]{\mathrm{Fe(CO)_5(cat.)\text{-}Co_2(CO)_8(cat.),\ NaOH\ aq./PhH:EtOH}} \mathrm{PhCOONa} \qquad (2)$$

In this biphasic system, ethanol was used to solubilize $[NBu_4]^+[HFe(CO)_4]^-$ in the organic upper layer. This complex is insoluble in water and only sparingly soluble in benzene, but under the basic conditions used, the presence of ethanol enables almost quantitative extraction of this salt into the organic layer.

We now report that under similar conditions, but in the absence of ethanol, $Fe(CO)_5$ and, better, $Fe(CO)_5$–$Co_2(CO)_8$ combinations can bring about the catalytic conversion of iodobenzene into mixtures of carbonylation products from which benzophenone can be isolated in fair yield (eq. 3).



$$\mathrm{PhI} \xrightarrow[\mathrm{NBu_4Br,\ CO(1\ atm),\ 65\,^\circ C}]{\mathrm{Fe(CO)_5(cat.)\text{-}Co_2(CO)_8(cat.),\ NaOH\ aq./PhH}} \mathrm{Ph{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}Ph + PhCOONa} \qquad (3)$$

Results

The main results are summarized in Table 1. As previously reported [16], in the presence of ethanol (run 1, conditions A) the bimetallic system is effective for the catalytic carbonylation of iodobenzene to give benzoic acid. In the absence of EtOH (conditions B), the anionic ironcarbonyl species, in association with the ammonium cation, are almost insoluble, and appear as an orange material at the interface of the two phases. (The IR spectra of the organic layer show the presence of small amounts of $[NBu_4]^+[HFe(CO)_4]^-$.) Nevertheless, even in the absence of cobalt species, this reaction medium allows the conversion of iodobenzene into a mixture of benzoic acid, benzophenone, and biphenyl, among which benzophenone is the major product (runs 2,3). (Traces of benzaldehyde are formed; the reduction product, benzene is also probably formed [15].) However, when the reaction is conducted in the presence of both iron and cobalt carbonyl species, a faster conversion occurs and higher yields of benzophenone are obtained (runs 4,5). The result of run 6 confirms that $Co(CO)_4^-$ alone promotes the conversion to give

Table 1

Carbonylation of C_6H_5I under carbon monoxide (1 atm) [a]

Run	Conditions [b]	$Fe(CO)_5$ (mmol)	$Co_2(CO)_8$ (mmol)	Reaction time (h)	Conv. (%) [c]	PhCOOH (%) [d]	PhC(O)Ph (%) [c]	PhPh (%) [c]
1	A	0.9	0.25	23	85	80	2	2
2	B	0.9	–	23	55	5	20	13
3	B	0.9	–	65	80	18	33	20
4	B	0.9	0.13	23	80	13	30	10
5	B	0.9	0.25	23	83	12	45	8
6	B	–	0.25	23	30	25	–	traces
7	C	1.8	0.50	23	95	30	50 [d]	6

[a] Reactions conducted at 65 °C under phase transfer conditions, 750 rpm. [b] Conditions: A: NaOH (6.5 g); H_2O: 20 ml; benzene: 20 ml; EtOH: 10 ml; NBu_4Br: 1.5 mmol; C_6H_5I: 10 mmol; B: NaOH (6.5 g); H_2O: 20 ml; benzene: 20 ml; NBu_4Br: 1.5 mmol; C_6H_5I: 10 mmol; C: NaOH (16.3 g); H_2O: 50 ml; benzene: 30 ml; NBu_4Br: 3 mmol; C_6H_5I: 20 mmol. [c] Determined by GLC with internal standards. [d] Isolated yield after column chromatography and recrystallisation.

exclusively benzoic acid [16]. Thus, a synergetic effect is observed between iron and cobalt carbonyl species for the formation of benzophenone (compare runs 2, 5 and 6). Finally, although the $Fe(CO)_5/Co_2(CO)_8$ ratio was not optimised, benzophenone was isolated in 50% yield (run 7), i.e. with a benzophenone/$Fe(CO)_5$ ratio of 3 and a benzophenone/$Co_2(CO)_8$ ratio of 10. To the best of our knowledge, this transition-metal catalysed synthesis of benzophenone directly from iodobenzene is unprecedented.

The reaction was also applied to some substituted aryl iodides under the most efficient conditions identified to date. The main results are shown in Table 2. Although the reaction conditions were not optimized, some substituted benzophenones were obtained in fair yields. In some cases, however, there is serious competition from formation of either the aromatic acid (runs 11, 12, 13) or the reduction product (run 13). This observation is particularly the case for aryl iodides bearing a chlorine substituent, 1,2 chloroiodobenzene giving only traces of the corresponding benzophenone. Even so this reaction may be worth studying as a new route to symmetri-

Table 2

Carbonylation of RC_6H_4I under carbon monoxide (1 atm) [a]

Run	R	Reaction time (h)	Conv. (%) [b]	ArCOOH (%) [c]	ArC(O)Ar (%) [d]	ArCHO (%) [c]	ArH (%) [b]	ArAr (%) [e]
8	H	23	95	30	50	traces		6
9	*p*-Me	48	98	20	57	6	8	6
10	*p*-MeO	48	95	15	55	10	10	2
11	*p*-Cl	60	95	35	30	traces	25	4
12	*m*-Me	24	98	60	30	traces	6	2
13	*m*-Cl	48	88	27	20	traces	37	4
14	*o*-Me	48	82	15	47	traces	15	3

[a] Reactions conducted at 65 °C under phase transfer conditions (750 rpm): ArI (20 mmol); $Fe(CO)_5$ (1.8 mmol); $Co_2(CO)_8$ (0.5 mmol); NaOH (16.3 g); H_2O: 50 ml; benzene: 30 ml; NBu_4Br: 3 mmol. [b] Determined by GLC with decane as internal standard. [c] Isolated yield. [d] Isolated yields after column chromatography and recrystallisation. [e] Contaminated by residual traces of ArI and ArH.

cal diaryl ketones. Work is in progress aimed at gathering more information about the mechanism of these reactions and determining the scope and limitations of bimetallic systems involving iron pentacarbonyl.

Experimental

General

All experiments were carried out under a well-ventilated hood. Manipulations of air-sensitive iron and cobalt complexes were performed under argon by standard Schlenk tube techniques. Argon U (L'Air Liquide) and carbon monoxide (N20, L'Air Liquide) were used. Thiophene-free benzene (Aldrich), absolute ethanol (Prolabo, Normapur), $Fe(CO)_5$ (Aldrich), $Co_2(CO)_8$ (Strem Chemicals), NaOH (Prolabo) and Bu_4NBr (Fluka) were used without further purification. All aryl iodides (Fluka or Lancaster Synthesis Ltd) were purified before use by either distillation or recrystallisation. Analytical thin-layer chromatography was carried out on silica gel 60 F_{254} plates. Preparative column chromatography was carried out on silica gel (60–200 mesh) from Merck.

IR spectra were obtained on a Perkin Elmer Model 597 spectrometer using CaF_2 (0.05 mm) windows. ^1H NMR spectra were recorded on a Bruker WH 90 spectrometer. Elemental analyses were performed at the Centre de Microanalyse of the CNRS.

Reactions were monitored by GLC on a Girdel 330 and an Intersmat IGC 121 gas chromatographs (flame ionization detectors) equipped with a 50 m capillary column (OV1, on-column injector), and a 3 m SE 30 (10%) column, respectively. In each case, peak areas were determined by use of a Spectra Physics SP 4290 computing integrator.

General procedure

General procedure (Table 1, run 7, and Table 2): A mixture of solution of sodium hydroxide (16.3 g) and NBu_4Br (0.965 g) in water (50 ml) with benzene (30 ml) was deaerated by bubbling argon through for 0.5 h. Iron pentacarbonyl (0.35 g) was then syringed in the reaction flask. After 0.5 h stirring at room temperature, dicobaltoctacarbonyl (0.17 g) was added. After 0.5 h stirring, the aryl iodide (20 mmol) and decane (as internal standard) were added. The flask was then connected to a gas buret filled with carbon monoxide and kept at 65 °C in an oil bath (with stirring at 750 rpm). At the end of the reaction (see reaction times in the Tables 1 and 2), the aqueous phase was separated, washed three times with diethyl ether, and filtered. Acidification with dilute HCl and extraction with ether afforded the aromatic acid, which was washed with 5% aqueous sodium thiosulfate and dried over sodium sulfate. The organic phases were combined and evaporated. The products were then separated by column chromatography on silica gel (with hexane–ether mixtures as eluents). The isolated benzophenones gave satisfactory elemental analyses, and were identified by comparison of their spectroscopic properties (IR, ^1H NMR) with literature data [20–22].

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