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CATALYTIC PHASE TRANSFER CARBONYLATION OF BENZYL HALIDES WITH IRON PENTACARBONYL.

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SUMMARY

Benzyl halides are readily carbonylated to arylacetic acids in a two-phase system (aqueous sodium hydroxide (1M), tetrabutylammonium sulfate ; organic phase (CH_2Cl_2 or C_6H_6 or $C_6H_5CH_3$)), using a catalytic amount of the cheap, easy to handle iron pentacarbonyl under carbon monoxide atmosphere.

Transition metal carbonyl-induced carbonylation of organic halides (reaction (1)) is of considerable interest in synthesis[1] :

$$RX \xrightarrow[CO]{M_x(CO)_y} RCO_2H \qquad (1)$$

Among the most successful metal carbonyl catalysts are dicobalt-octacarbonyl and nickel tetracarbonyl used in homogeneous[1,2] or liquid-liquid two-phase systems[3,4,5].

Concerning iron pentacarbonyl, less expensive and easier to handle, several strategies have been designed[6,7,8,9]. All these methods suffer from the fact that they are stoichiometric with respect to iron pentacarbonyl, and operate under rather drastic conditions (a dry medium[6,8,9] ; or high concentrations of sodium hydroxide in a two phase system under nitrogen, giving only ketones RCOR instead of RCO_2H[7] ; or prior and tedious synthesis of the tetracarbonyl ferrate dianion $Fe(CO)_4^{--}$ followed by the addition of the halide and further destructive oxidation[8], giving only moderate yields of phenylacetic acid when benzyl halides are used[9]).

We have found that benzyl halides can be carbonylated to phenylacetic acids in good yields using a liquid-liquid phase transfer system in which iron pentacarbonyl is introduced in catalytic amounts under carbon monoxide atmosphere

$$\underset{\underline{1}}{RX} \xrightarrow[\substack{\text{aqueous phase} \\ \text{NaOH, } (Bu_4N^+)_2SO_4^{--}}]{\text{organic phase, } Fe(CO)_5\text{, CO}} \underset{\underline{2}}{RCO_2H} \qquad (2)$$

Experimental conditions are very mild : moderate temperature, no need for an aprotic medium, low concentration of base (NaOH 1M), and, in several cases, one atmosphere of carbon monoxide. The following run is typical : into a two-phase system consisting of 10 mL aqueous sodium hydroxide (1M) and 10 mL of an organic solvent (CH_2Cl_2 or benzene or toluene), are introduced, under carbon monoxide atmosphere : 0.5 mmol $Bu_4N^+HSO_4^-$, 2.5 mmol of the halide. Then $Fe(CO)_5$ (0.25 mmol) is introduced with vigourous stirring (> 1200 r.p.m.). After several hours depending on the halide, the arylacetic acid 2 is extracted from the aqueous layer after acidification, and neutral by-products 3, 4, 5 and 6 are isolated and characterized (GC, ^1H NMR, MS) from the organic layer.

Results given in Table I for a number of halides desserve several comments. First, the reaction is truly catalytic : in run 4, the $Fe(CO)_5/RX$ ratio is 1/50 and almost the same yields are obtained as in run 2 ($Fe(CO)_5/RX$ 1/10). The reaction is not limited to bromides but also works for chlorides (runs 6, 12, 13, 14). Run 5 shows that a two-phase system is required for a successful reaction : in a homogeneous medium (CH_3OH), the yield of phenylacetic acid is very poor (7 %). Runs 3 and 15 make comparisons with a similar system under the same experimental conditions, but using the tetracarbonyl cobaltate anion instead of iron pentacarbonyl : it is shown that the iron carbonyl system is superior to the cobalt carbonyl one with respect to the carboxylation reaction. To conclude, we give a brief account of a possible catalytic cycle, which will be discussed in detail in a separate paper[10]. First, in this two phase system, even with the moderate concentration of sodium hydroxide used here

Table I

n°	RX 1	Catalytic medium	Catalyst and |Catalyst|/|RX|	T°C	PCO Atm.	Reaction time (hours)	Yields*				
							RCO_2H 2	RCO_2R** 3	RCOR 4	RR 5	RH 6
1	$C_6H_5CH_2Br$	H_2O/C_6H_6	$Fe(CO)_5$ 1/10	20	1	15	75	3	14	6	2
2	"	H_2O/CH_2Cl_2	"	20	1	3,5	73	6	12	6	
3	"	"	$Fe(CO)_5$ 1/20	20	1	20	69	7	20	3	
4	"	"	$Fe(CO)_5$ 1/50	25	60	27	66	8	11	4	
5	"	CH_3OH	$Fe(CO)_5$ 1/10	50	60	8	7***				
6	$C_6H_5CH_2Cl$	H_2O/toluene	"	50	60	29	61	2	4	7	
7	$mCH_3C_6H_4CH_2Br$	H_2O/CH_2Cl_2	"	25	1	24	54	15	27	5	
8	$oCH_3C_6H_4CH_2Br$	"	"	25	1	24	69	18	7	10	
9	$mCNC_6H_4CH_2Br$	"	"	25	60	21	43****				
10	$pBrC_6H_4CH_2Br$	"	"	25	1	24	50	22	9	7	
11	β-Naphtyl-CH_2Br	H_2O/toluene	"	60	60	53	55				
12	$mCH_3C_6H_4CH_2Cl$	"	"	60	60	47	31†	9	8		
13	oo'p$(CH_3)_3$-$C_6H_2CH_2Cl$	"	"	60	60	26	37††	11	5		
14	$mCH_3OC_6H_4CH_2Cl$	"	"	50	60	51	35†††				
15	$C_6H_5CH_2Br$	H_2O/CH_2Cl_2	$NaCo(CO)_4$ 1/20	20	1	40	9	3	12	50	20

* in % based on benzyl halide introduced.

** these esters 3 come from a slow phase transfer reaction between the remaining halide and the carboxylate anion produced.

*** the main product is $C_6H_5CH_2OCH_3$, resulting from the Williamson synthesis.

**** $mCO_2HC_6H_4CH_2CO_2H$ obtained.

† 15 % of the halide unreacted.

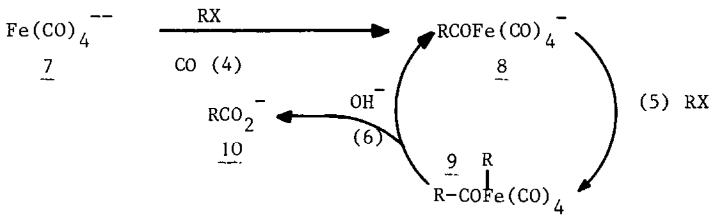
†† 21 % of the halide unreacted.

††† 61 % of the halide unreacted.

(1 M), iron pentacarbonyl gives the tetracarbonyl ferrate dianion 7 (reaction (3)). This point has been firmly established in separate experiments[10].

$$Fe(CO)_5 \xrightarrow[\text{two phase system}]{OH^-} \underset{7}{Fe(CO)_4^{--}} + CO_2 + H_2O \qquad (3)$$

Then, this anion quickly reacts with the benzyl halide according to the following cycle :



Reactions (4) and (5), occuring in the organic layer, have been demonstrated already under homogeneous conditions in the absence of a base[11] : they normally give ketone 4 through the decomposition of the unstable organometallic 9. Here, reaction (6), occuring at the liquid-liquid interface[12], is faster and gives the carboxylate anion 10, which is expelled in the aqueous phase.

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