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Normal Pressure Double Carbonylation of Aryl Halides Using Cobalt(II) Chloride in the Presence of either Sodium Sulfide or Sodium Borohydride

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Synopsis. Tetracarbonylcobaltate ion generated by a treatment of cobalt(II) chloride with either sodium sulfide or sodium borohydride under a normal pressure of carbon monoxide was capable of catalyzing carbonylation of aryl halides in the presence of calcium hydroxide and methyl iodide to give arylglyoxylic acids in good selectivity.

Several effective methods for cobalt-catalyzed carbonylation of aryl halides to produce the corresponding carboxylic acids, α-keto carboxylic acids, and alkyl aryl ketones have recently been developed, using either tetracarbonylcobaltate ion $Co(CO)_4^-$ under photostimulation[1,2] or alkyltetracarbonylcobalt complexes $RCo(CO)_4$.[3,4] In the latter case, we reported that the product distribution is a marked function of the solvent system employed.[4] These reactions smoothly proceed in the presence of an appropriate base under extremely mild conditions. The catalytically active species are usually prepared in situ from somewhat air-sensitive octacarbonyldicobalt $Co_2(CO)_8$. Simple inorganic cobalt salts have also been successfully used as the catalyst precursors;[5—7] however only the monocarboxylic acids were isolated.

As part of our study, we have undertaken the synthesis of the α-keto carboxylic acids using cobalt salts in order to provide a convenient route to the acids.[8] We observed that the tetracarbonylcobaltate ion prepared by a treatment of cobalt chloride with either sodium sulfide in water[9] or sodium borohydride in dioxane[10] can catalyze the carbonylation of aryl halides (**1**) at room temperature under a normal pressure of carbon monoxide to give the corresponding α-keto acids (**2**) in good selectivity along with the glycolic acids (**3**) and the mono acids (**4**) (Eq. 1 and Table 1).[11]

$$\underset{\mathbf{1}}{\mathrm{ArX}} \xrightarrow[\mathrm{Na_2S\ or\ NaBH_4/Ca(OH)_2}]{\mathrm{CO/CoCl_2/MeI}} \underset{\mathbf{2}}{\mathrm{ArCOCOOH}} + \underset{\mathbf{3}}{\mathrm{ArCH(OH)COOH}} + \underset{\mathbf{4}}{\mathrm{ArCOOH}} \qquad (1)$$

1a: 1-bromonaphthalene
1b: bromobenzene
1c: iodobenzene

Table 1. Carbonylation of Aryl Halides with Cobalt Chloride[a]

Run	**1** (mmol)	Co-catalyst	Solvent[b]	Conv./%	Product yield/%[c]		
					2	**3**	**4**
1	**1a** (5)	Na_2S	A	51	86	9	4
2	**1a** (10)[d]	Na_2S	A	41	87	5	4
3	**1a** (5)	$NaSCH_3$	A	20	75	5	17
4	**1a** (10)	$NaBH_4$	A	39	80	3	5
5	**1a** (5)	—[e]	A	55	85	4	5
6	**1a** (5)	Na_2S	B	90	89	3	6
7	**1a** (10)	Na_2S	B	53	89	4	7
8	**1a** (10)	Na_2S	B[f]	31	88	7	2
9	**1a** (10)	Na_2S	B[g]	31	82	3	10
10	**1a** (5)[h]	Na_2S	B	11	20	17	60
11	**1b** (5)	Na_2S	A	42	53[i]	4	5
12	**1b** (5)	$NaBH_4$	A	40	57[i]	2	8
13	**1b** (5)	Na_2S	B	74	48[i]	2	8
14	**1c** (5)	Na_2S	A	61	62[i]	3	5
15	**1c** (5)	$NaBH_4$	A	48	68[i]	3	5
16	**1c** (5)	Na_2S	B	78	64[i]	3	13

a) The reaction was carried out using $CoCl_2$ (0.5 mmol), Na_2S (0.25 mmol) or $NaBH_4$ (1 mmol), $Ca(OH)_2$ (35 mmol), and methyl iodide (25 mmol) at 20 °C for 20 h. b) A: Dioxane-H_2O (3 : 1, v/v). B: 2-Propanol-H_2O (1 : 1, v/v). c) Yield based on the halide consumed was determined by GLC after trimethylsilylation with *N,O*-bis(trimethylsilyl)acetamide or methylation with diazomethane. d) Reaction for 40 h. e) $Co_2(CO)_8$ (0.25 mmol). f) 2-Propanol-H_2O (3 : 1, v/v). g) 2-Propanol-H_2O (1 : 2, v/v). h) Reaction at 60 °C. i) The keto acid was obtained as a mixture of the acid and the condensated product with pyruvic acid. The value indicates that after hydrolysis of the product mixture with NaOH.[3,4]

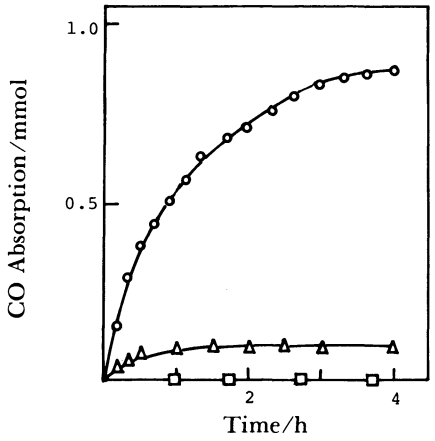

Fig. 1. CO Absorption in the treatment of $CoCl_2$ (0.5 mmol) with sulfur-containing compounds in the presence of $Ca(OH)_2$ (35 mmol): Na_2S (0.25 mmol) ○, $NaSCH_3$ (0.5 mmol) △, and $C_2H_5OCS_2K$ (0.5 mmol) □.

When cobalt chloride (0.5 mmol) was treated with sodium sulfide (0.25 mmol) in the presence of calcium hydroxide in water at 20 °C under carbon monoxide (1 atm) for 4 h, about 0.9 mmol of carbon monoxide was consumed (Fig. 1). The IR spectrum of the solution showed a single characteristic peak for $Co(CO)_4^-$ at 1913 cm^{-1} in the region 1700 to 2000 cm^{-1}. The addition of **1** (5 or 10 mmol) in dioxane, together with methyl iodide to the solution, gave **2** along with **3** and **4**. The formation of aryl methyl ketone was not detected in each reaction. The conversion of **1** and the selectivity of **2** were comparable with those using $Co_2(CO)_8$ (0.25 mmol) (Runs 1 and 5). Cobalt sulfide could not be used in place of $CoCl_2$–Na_2S, suggesting that the sulfide does not participate in the formation of the active species. While sodium methanethiolate, which is an efficient reagent for the preparation of nickel(0) carbonyl derivatives from nickel chloride,[12] could also be used in place of sodium sulfide, it was considerably less effective than the sulfide (Run 3 and Fig. 1). Potassium ethylxanthogenate and sodium diethyldithiocarbamate were ineffective.

As an alternative catalyst system for the carbonylation, $CoCl_2/NaBH_4/Ca(OH)_2$ could also be successfully used (Runs 4, 12, and 15). In this case, the cobaltate ion was prepared within 1.5 h (see Experimental).

It is noteworthy that, in the reaction in 2-propanol–water (1:1, v/v), a remarkably higher conversion of **1**, accompanied by a little decrease of the selectivity of **2**, was observed (Runs 6, 13, and 16). This is in contrast with the reactions in dioxane–water (1:1) and ethanol–water (1:1) in which the mono acids **4** were the major products.[4] The conversion of **1**, however, decreased as a result of changes in the 2-propanol–water ratio from 1:1 to both 3:1 and 1:2 (Runs 8 and 9).

In conclusion, the double carbonylation reaction of aryl halides to give arylglyoxylic acids was conveniently carried out using only simple reagents which are inexpensive and easily handled.

Experimental

Generation of Tetracarbonylcobaltate Ion. (a) To a flask containing cobalt chloride (0.5 mmol), sodium sulfide nonahydrate (0.25 mmol), and calcium hydroxide (35 mmol) was added water (10 cm^3). The mixture was stirred for 4 h at room temperature under carbon monoxide (1 atm). (b) A mixture of cobalt chloride (0.5 mmol) and sodium borohydride (1 mmol) in dioxane (10 cm^3) was stirred at 20 °C for 1 h, while bubbling carbon monoxide. Then, water (5 cm^3) and calcium hydroxide (35 mmol) were added and stirred for a further 20 min.

Carbonylation of Aryl Halides 1 and the Product Analysis. The methods were essentially the same as those described previously.[4]

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