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Chemoselectivity of cobalt-catalysed carbonylation—A reliable platform for the synthesis of fluorinated benzoic acids

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ABSTRACT

The cobalt-catalysed methoxycarbonylation of polysubstituted bromo,fluoro- and chloro,fluorobenzenes and 1,2,4-trichlorobenzene with emphasis on the chemo- and regio-selectivity of the reaction is described. The structures of isolated products of 1,4-dichloro-2-fluorobenzene carbonylation were determined by single-crystal X-ray diffraction. The fact that the fluorine substituents in the studied compounds remain intact indicates in favor of the anion-radical activation of aryl halides by a cobalt catalyst. For the first time, a universal method of preparation of the various fluorobenzoic acid derivatives from available raw materials with a good yield has been elaborated.

1. Introduction

The carbonylation of primary and secondary alkylhalides, benzyl halides, and their derivatives is one of the well-investigated carbonylation reactions catalysed by transition metals. The reaction occurs in the presence of tetracarbonylcobaltate anion and corresponds to the S_N2 mechanism [1–4]. The activation of aryl halides requires special techniques, including the UV irradiation, the system enrichment with a one-electron reducing agent, or the modification of the $Co(CO)_4^-$ anion [5–14]. All these early studies demonstrate the ability of the $Co(CO)_4^-$ anion to be an efficient catalyst for the carbonylation of aryl halides in conditions that provide the anion-radical synthetic pathway. This mechanism can occur because cobalt carbonyl complexes form a system with an open electron shell (radicals) relatively easy [15,16].

Alongside with the others, we have studied the reaction of the aryl halide carbonylation catalysed by a modified cobalt carbonyl complex (Scheme 1) [11–14].

Thereupon, the study of chemoselectivity is of interest for carbonylation of polyhalogenated bromo,fluoro- and chloro,fluorobenzenes. The key stage of carbonylation process is the reaction between an aryl halide and an anionic cobalt complex leading to the formation of an aryl cobalt complex in the reaction of nucleophilic substitution [13]. This reaction can proceed in several different ways, two of which are potentially relevant in this system: the classic S_NAr mechanism (*via* intermediate formation of a Meisenheimer complex) or the radical-anion nucleophilic substitution ($S_{RN}1$) involving the electron transfer from the cobalt anionic complex to the aryl halide. We have demonstrated [13] the definite evidence in favor of the $S_{RN}1$ mechanism. The chemoselectivity data of fluorinated aryl halide carbonylation could answer the question of actual mechanism of this interaction. As a rule, the S_NAr nucleophilic substitution reveals an increased reactivity of the corresponding fluorides compared to both bromides and chlorides. For example, the reaction between sodium benzylate and either 2-bromofluorobenzene or 2-bromo-6-fluorotoluene results in the alcoholysis products at fluorine atoms with a yield of 94–95% [17]. At the same time, the $S_{RN}1$ mechanism differs fundamentally from the standard S_NAr one; in particular, aryl fluorides are less reactive in that sort of reactions than either aryl chlorides or aryl bromides; commonly, they are not exposed to nucleophilic substitution [18].

Along with the theoretical importance, the data on carbonylation of mixed fluoro,halobenzenes are of significant practical concern. We have successfully applied [11] this modern approach for the synthesis of some fluorinated benzoic acids **1**–**4** (Chart 1).

The application of cobalt-catalysed carbonylation for the synthesis of fluorosubstituted phenylacetic acids and esters has

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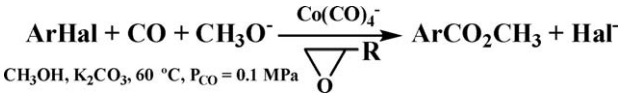


Scheme 1. General scheme of carbonylation reaction.

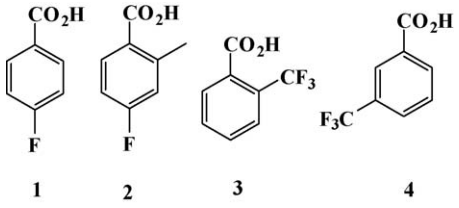


Chart 1.

been studied [3]. However, the description of the preparation of different fluorinated benzoic acids (except 4-fluorobenzoic acid) has not been published until 2007 [11].

Comparison of our preparative results [11] with the reported routes for the synthesis of these products [19–22] revealed that a universal method of synthesis of different fluorosubstituted benzoic acids from available raw materials with good yields has been elaborated for the first time. High selectivity of carbonylation of these substrates (95–100%) and excellent preparative yields (85–95%) can serve in favor of $S_{RN}1$ mechanism.

2. Results and discussion

To finally clarify on the relative reactivity of different halides in the reaction of cobalt-catalysed carbonylation, we carried out carbonylation of 1,4-dichloro-2-fluorobenzene **5**. It is known [23] that the reaction between 1,2-dichloro-4-fluorobenzene and methylate-anion exclusively yields 3,4-dichloroanisole. It means that only the fluorine atom is subjected to the S_NAr attack while the chlorine atoms remain intact. In our case, at the first stage of the reaction, one would expect the formation of either **6** or a mixture of **7** and **8** depending on the mechanism of the nucleophilic substitution in the system (Scheme 2).

The cobalt-catalysed carbonylation was carried out under the synthetic conditions elaborated in [11]: atmospheric pressure of carbon monoxide, a temperature of 61–63 °C, the methanol/potassium carbonate/potassium tetracarbonylcobaltate system. Methyloxirane was used as a modifier. A short-time process and low concentrations of reactants and catalyst provide an insignificant conversion of the substrate (15–30%) at the first stage of the reaction. The substituted methylbenzoates as the reaction products were isolated from the reaction mixture using extraction and column chromatography. An additional methylation of the reaction mixture (see the experimental part) was carried out to avoid the loss of the partially hydrolysed products.

The structures of the isolated products were determined by single-crystal X-ray diffraction to exclude any doubts in the real reaction pathway. The experiment showed that cobalt-catalysed carbonylation of 1,4-dichloro-2-fluorobenzene **5** resulted in

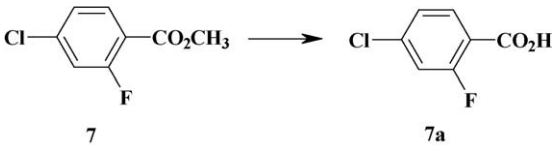


Chart 2.

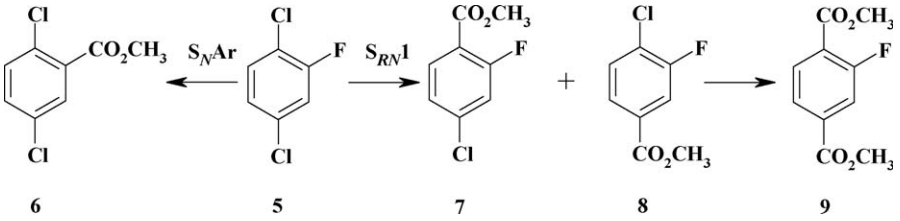
Table 1
Crystal data and structure refinement parameters for **7a** and **9**.

	7a	**9**
Empirical formula	$C_7H_4ClFO_2$	$C_{10}H_7FO_4$
Formula weight	174.55	210.16
Crystal system	Triclinic	Monoclinic
Space group	*P-1*	$P2_1/n$
Unit cell dimensions		
a (Å)	3.8432(3)	3.9806(5)
b (Å)	6.3360(4)	6.1966(11)
c (Å)	14.3645(10)	19.146(4)
α (deg)	86.146(6)	90
β (deg)	85.281(6)	94.037(15)
γ (deg)	89.904(6)	90
V (Å^3)	347.81(4)	471.08(13)
Z	2	2
D_{calc} (g/cm^3)	1.667	1.482
μ (mm^{-1})	4.588	0.128
$F(000)$	176	216
Reflections collected/unique	16108/1361	5836/916
R(int)	0.0556	0.0214
Reflections with $[I > 2\sigma(I)]$	1182	810
Data/restraints/parameters	1361/0/110	916/0/83
Goodness-of-fit on F^2	1.120	1.096
Final R indices $[I > 2\sigma(I)]$ R_1, wR_2	0.0459, 0.1327	0.0340, 0.0998
R indices (all data) R_1, wR_2	0.0515, 0.1443	0.0382, 0.1026

methyl 4-chloro-2-fluorobenzoate **7** and dimethyl 2-fluoroterephthalate **9**. Since compound **7** was oil, we have saponified it and obtained single crystals of compound **7a** suitable for X-ray analysis (Chart 2, Section 2).

The crystal structure and refinement data are given in Table 1. Selected bond distances and angles are summarised in Table 2. Compounds **7a** and **9** crystallise in triclinic (space group *P-1* with $Z = 2$) and monoclinic (space group $P2_1/n$ with $Z = 2$) crystal systems, respectively. The asymmetric molecule **7a** occupies a general position while **9** resides on an inversion center (Fig. 1).

Molecule **7a** is characterised by the planar skeleton with the carboxylic group being near coplanar to the aromatic ring: the dihedral angle between the carboxylic group and the aromatic ring is 6.1(3)°. Similar to the previously reported fluorinated benzoic acids which easily form either the homo- or hetero-dimers [24], two centrosymmetric single O–H···O hydrogen bonds [H···O1($-x$, $-y+1$, $-z+2$) 1.69(5), O2···O1($-x$, $-y+1$, $-z+2$) 2.716(3) Å, angle O–H···O 174(4)°] combined into robust $R_2^2(8)$ synthon [25] govern the packing of the *molecules into* planar dimers. The dimers



Scheme 2. Possible synthetic pathways of the nucleophilic substitution.

Table 2
Selected interatomic distances (Å) and angles (°) for **7a** and **9**.

	7a	9
Cl(1)–C(5)	1.796(2)	–
F(1)–C(3)	1.329(3)	1.301(3)
O(1)–C(1)	1.235(3)	1.205(2)
O(2)–C(1)	1.301(3)	1.333(2)
O(2)–C(5)	–	1.453(2)
C(1)–C(2)	1.540(3)	1.497(2)
C(2)–C(7)	1.381(3)	–
C(2)–C(3)	1.399(3)	1.398(2)
C(2)–C(4)	–	1.393(2)
C(3)–C(4)	1.426(3)	1.385(2)
C(4)–C(5)	1.371(3)	–
C(5)–C(6)	1.384(3)	–
C(6)–C(7)	1.429(3)	–
O(1)–C(1)–O(2)	121.0(2)	124.0(1)
C(1)–O(2)–C(5)	–	115.5(1)
O(1)–C(1)–C(2)	120.8(2)	123.6(1)
O(2)–C(1)–C(2)	118.2(2)	112.4(1)
C(7)–C(2)–C(3)	113.8(2)	–
C(7)–C(2)–C(1)	121.6(2)	–
C(3)–C(2)–C(1)	124.5(2)	122.7(1)
C(4)–C(2)–C(1)	–	118.4(1)
C(4)–C(2)–C(3)	–	118.9(1)
F(1)–C(3)–C(2)	118.4(2)	123.6(2)
F(1)–C(3)–C(4)	116.9(2)	115.8(2)
C(2)–C(3)–C(4)	124.8(2)	120.3(1)
C(5)–C(4)–C(3)	118.9(2)	–
C(3)#1–C(4)–C(2)	–	120.8(1)
C(4)–C(5)–C(6)	118.9(2)	–
C(4)–C(5)–Cl(1)	119.3(2)	–
C(6)–C(5)–Cl(1)	121.7(2)	–
C(5)–C(6)–C(7)	120.4(2)	–
C(2)–C(7)–C(6)	123.2(2)	–

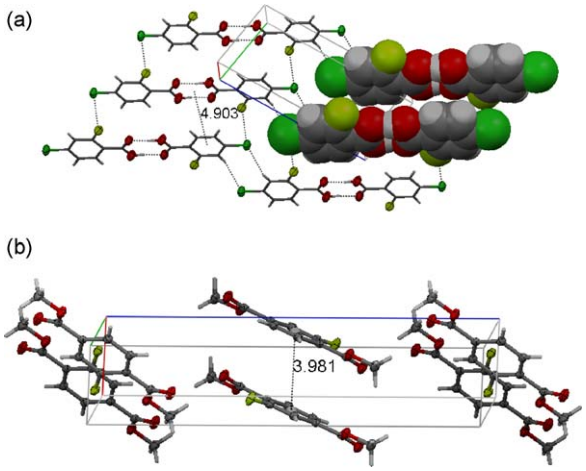


Fig. 2. Fragment of crystal packing in **7a** (a) and **9** (b).

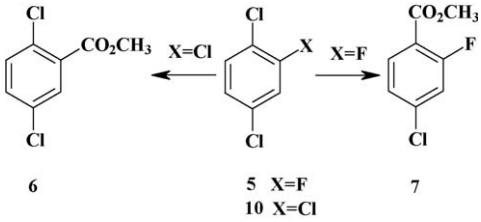


Chart 3.

stack along the shortest crystallographic *a* direction with the distance of 4.903 Å between the centroids of the aromatic and the hydrogen-bonded $R_2^2(8)$ supramolecular rings. The interhalogen F···Cl interactions [26,27] of 3.157 Å, alongside with the C–H···F (C···F 3.544 Å) short contacts acting approximately orthogonally [28] to the plane of the above-mentioned hydrogen bonds, direct the herringbone assembling of the adjacent stacks (Fig. 2a). In **9**, the methoxy-group forms a dihedral angle of 14.9° with the aromatic ring. Similar to **7a**, the packing of the molecules is mediated by the π–π stacking interactions along the shortest *a* axis with the distance of 3.981 Å between the centroids of the inversion-related molecules (Fig. 2b).

Upon carbonylation of compound **5** under the reaction conditions, products of fluorine substitution were not observed. The carbonylation of 1,2,4-trichlorobenzene **10** carried out under the same conditions occurs in position 2 and leads to methyl 2,5-dichlorobenzoate **6** as a major product (Chart 3).

This means that the selectivity of carbonylation of compound **5** is predominantly determined by the nature of halogen rather than by the relative positions of substituents in the aromatic ring. The fact that the fluorine atoms in **5** remain intact to carbonylation clearly indicates in favor of the anion-radical activation of aryl halides by a cobalt catalyst.

In conclusion, the high selectivity of cobalt-catalysed carbonylation is dictated by the anion-radical mechanism of aryl halide activation by a modified cobalt carbonyl complex. It allows using this effective procedure as a universal method of synthesis of fluorinated benzoic acids.

3. Experimental

NMR spectra were recorded by a Bruker DPX 300. Commercially available organic and inorganic reagents (chemically pure grade) were used without further purification. Potassium carbonate (p.a.) was dried at 150 °C for 6 h. Cobalt carbonyl was a commercial reagent (Merck & Co).

3.1. Preparation of potassium tetracarbonylcobaltate $KCo(CO)_4$ solution with known concentration

Potassium carbonate (1.0 g, 7.2 mmol) and methanol (8 mL) were placed in a Shlenk flask. The intensively stirred mixture was

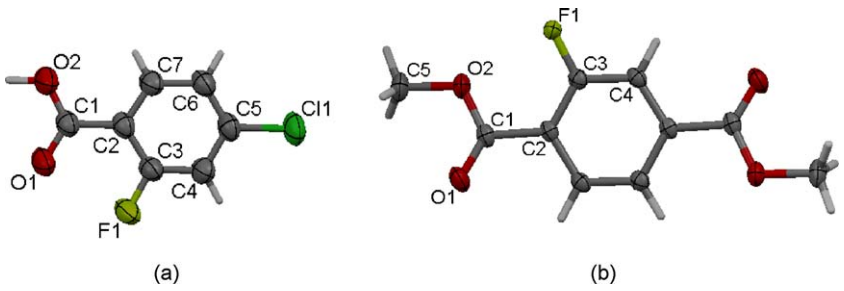


Fig. 1. ORTEP drawing for **7a** (a) and **9** (b). Only the asymmetric unit is labeled.

subjected to a flow of carbon monoxide at room temperature for 10 min followed by the insertion of $Co_2(CO)_8$ (0.5 g, *ca.* 1.5 mmol). The blow of CO through the intensively stirred solution was stopped after disappearance of the orange color that indicated in favor of the tetracarbonylcobaltate salt formation according to the reaction:

$$3Co_2(CO)_8 + 2K_2CO_3 \rightarrow 4KCo(CO)_4 + 2CoCO_3 + 8CO$$

The concentration of cobalt in the transparent colorless solution obtained after removal of the precipitate was determined by oxidation of $KCo(CO)_4$ to Co(II) by nitric acid followed by EDTA titration (indicator murexide, pH 9, ammonia buffer).

3.2. General procedure of carbonylation

The stirred mixture of K_2CO_3 (2 g, 14 mmol), methanol (10 ml), and substrate (2 mmol) placed in a glass reactor with a jacket for the thermostatic experiment was bubbled for 0.5 h by carbon monoxide, which preliminary passed through methanol. Then the reaction flask was stopped with a rubber septum; a solution of $KCo(CO)_4$ in methanol (0.133 mmol, 0.7 mL of 0.19 M solution) was added by a syringe through the septum. The reaction mixture was heated up to 61 °C; methyloxirane (0.35 g, 6 mmol) was added by a syringe. The conversion was controlled by the measurement of carbon monoxide volume. After obtaining of the desired conversion, the reaction mixture was cooled till the room temperature, acidified with concentrated hydrochloric acid, and diluted with water; the reaction products were extracted by diethyl ether. The solvent was removed under a reduced pressure, the residue was dissolved in 10 mL of methanol cooled with a dry ice bath, and thionyl chloride (0.6 g, 5 mmol) was carefully added to the reaction mixture. The reaction mixture was kept at a room temperature for 1 h. Then the solvent and an excess of thionyl chloride were removed under a reduced pressure. The resulting mixture was analysed by the TLC and ^{1}H NMR method; then the carbonylation products were isolated by column chromatography (eluent: ethyl acetate–hexane, 1:5).

3.3. Carbonylation of 1,4-dichloro-2-fluorobenzene (**5**) at 30% conversion

3.3.1. Methyl 4-chloro-2-fluorobenzoate (**7**)

Yellow oil, R_f 0.37. Yield 75 mg (20%). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm), δ = 3.94 s (3H, CH_3), 7.15–7.24 m (2H), 7.87–7.95 m (1H). ^{13}C NMR ($CDCl_3$, 75.5 MHz, ppm), δ = 52.84 (OCH_3), 117.63 d, J = 10 (C; C-1), 118.14 d, J = 26 (CH; C-3), 124.98 d, J = 3 (CH; C-6), 133.46 (CH; C-5), 140.33 d, J = 11 (C; C-4), 161.97 d, J = 263 (C; C-2), 164.46 d, J = 4 (CO_2CH_3). For identification, **7** was saponified by a boiling solution of KOH (0.4 g) in methanol (10 ml) for 5 h. Methanol was removed, water (10 ml) was added, and the reaction mixture was acidified by HCl till pH < 1. The precipitate of 4-chloro-2-fluorobenzoic acid (**7a**) (60 mg) was filtered off and dried. M.p. = 205 °C (M.p. = 203–204 °C [29]). The single crystal suitable for X-ray study was obtained by recrystallisation from dichloromethane–hexane (1:1) mixture.

3.3.2. Dimethyl 2-fluoroterephthalate (**9**)

Solid, R_f 0.32. Yield 17 mg (4%). M.p. = 81 °C (M.p. = 82–83 °C [30]). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm), δ = 3.95 s (3H, CH_3), 3.96 s (3H, CH_3), 7.75–7.89 m (2H), 7.96–8.04 m (1H). ^{13}C NMR ($CDCl_3$, 75.5 MHz, ppm), δ = 53.03 (OCH_3), 53.08 (OCH_3), 118.51 d, J = 24 (CH; C-3), 122.84 d, J = 11 (C; C-1), 125.20 d, J = 4 (CH; C-6), 132.61 (CH; C-5), 136.13 d, J = 9 (C; C-4), 161.84 d, J = 261 (C; C-2), 164.59 (CO_2CH_3), 165.48 (CO_2CH_3).

3.4. Carbonylation of 2-fluoro-1,4-dichlorobenzene (**5**) at full conversion

3.4.1. Methyl 4-chloro-2-fluorobenzoate (**7**)

240 mg (64%).

3.4.2. Dimethyl 2-fluoroterephthalate (**9**)

76 mg (18%).

The crystals suitable for the X-ray experiment were obtained by crystallisation from the mixture ethylacetate–hexane, 1:5.

3.5. Carbonylation of 1,2,4-trichlorobenzene (**10**) at 30% conversion

3.5.1. Methyl 2,5-dichlorobenzoate (**6**)

Oil, R_f 0.39. Yield 45 mg (13%). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm), δ = 3.96 s (3H CH_3), 7.38–7.42 m (2H), 7.84 s (1H).

3.6. Structure determination

X-ray data for **7a** were collected with an Oxford Diffraction Super Nova diffractometer using Cu Kα radiation (λ = 1.5418 Å) at 130 K and for **9** with an Oxford Diffraction XcaliburE diffractometer using Mo Kα radiation (λ = 0.71059 Å) at 293 K [31]. Final unit cell dimensions were obtained and refined on the entire data set. The structures were solved by direct methods with *SHELXL-97* and refined against F^2 with *SHELXL-97* [32]. In **7a**, the fluorine atom is statistically distributed and alternates with H-atoms in *o*-positions to the carboxylic group with occupancies of 0.884(5) and 0.116(5), respectively, only the major position being treated in the anisotropic approximation. The carboxylic H-atom was determined from a difference Fourier map and refined freely. In **9**, the fluorine atom is statistically distributed and alternates with H-atoms in four *o*-positions to the methylcarboxylate group with occupancies of 0.29(5) and 0.21(5), respectively, only the major position being treated in the anisotropic approximation. The crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos CCDC 739708 and CCDC 739709. Copies of these data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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