

APPLIED ELECTROCHEMISTRY
AND CORROSION PROTECTION OF METALS

Synthesis of Aromatic Carboxylic Acids by Carbonylation
of Aryl Halides in the Presence of Epoxide-Modified Cobalt
Carbonyls as Catalysts

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Received July 19, 2005

Abstract—A new procedure was developed for synthesis of aromatic and heteroaromatic acids and their derivatives (esters, salts) by carbonylation of the corresponding aryl halides. The acids are selectively formed in a high yield under very mild conditions. Highly active catalytic systems, base-containing alcoholic solutions of cobalt carbonyl modified with epoxides, were used to activate aryl halides.

Aromatic acids and their derivatives (esters and salts) are widely used both in preparative organic chemistry and as commercial raw materials to produce pharmaceuticals, plant protecting agents, paint and varnish materials, lubricants, and corrosion inhibitors. In addition, aromatic carboxylic acids are used as the base of modern liquid-crystal materials. Di- and poly-aryl carboxylic acids are used in production of polyester fibers and liquid-crystal thermoplastics as well as electroluminophores in development of new equipment.

The conventional methods for preparing aromatic acids under industrial and laboratory conditions are different and involve classical organic reactions: alkylation, acylation, oxidation, and cyanidation. The disadvantages of these methods are their low selectivity and high consumption of raw materials. The synthesis is multistep and requires complex process schemes. Many of these methods are environmentally hazardous.

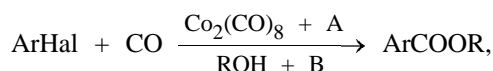
Recently, researchers turned attention to an alternative one-step selective procedure for preparing aromatic carboxylic acids: carbonylation of the corresponding aryl halides. Aryl halides are readily available and cheap. However, these compounds, especially the cheapest aryl chlorides, have low reactivity.

Originally, “soft” aryl halides (iodides and bromides) were used for this purpose. These compounds can be activated by oxidative addition to complexes of palladium in a low oxidation state [1–3].

At the same time, alkylaromatic halides are car-

bonylated under extremely mild conditions in alcohols in the presence of a base and conventional catalyst of oxosynthesis, octacarbonyldicobalt [1, 4, 5].

Alkylcobalt carbonyl complexes are formed *in situ* by the reaction of alkyl halides reactive in nucleophilic substitution (e.g., methyl chloroacetate) with dicobalt octacarbonyl in alcoholic solutions containing a base. These complexes can activate weakly active aryl halides, involving them in carbonylation [6]. In this case, alkyl halides are cocatalysts (activators) of cobalt carbonyl in carbonylation of aryl halides:



where A and B are cocatalyst and base, respectively.

The facts that acceptor substituents accelerate carbonylation of substituted bromobenzenes and one-electron acceptors (nitrobenzene and anthraquinone) inhibit carbonylation of aryl halides suggests radical anion mechanism of aryl halide activation ($S_{RN}1$). The actual carbonylation catalyst is, apparently, the anionic complex $[\text{RCo}(\text{CO})_3\text{COOCH}_3]^-$ formed by the nucleophilic attack of the carbon atom of one of the carbonyl groups by the methylate anion. The nucleophilic power of this complex is high. Since benzyl chloride is also carbonylated under these conditions, it was gradually fed by a special procedure to the reaction mixture to maintain the catalyst in the active form and to increase the conversion (see figure). A series of valuable aromatic acids were prepared by carbonylation of the corresponding aryl halides in

methanol in the presence of cobalt carbonyl–benzyl chloride–base catalytic system. This system is the most suitable for carbonylation of 5,6-dichloroacenaphthene to acenaphthene dicarboxylic acid used for preparing a valuable commercial product, 1,4,5,8-naphthalene-tetracarboxylic acid [9].

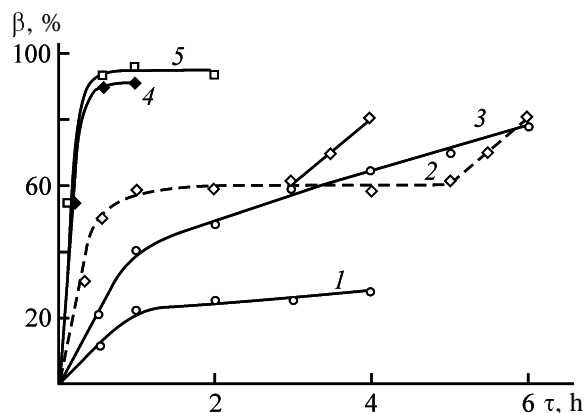
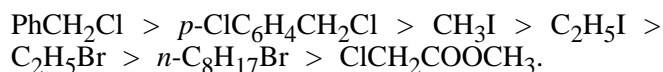
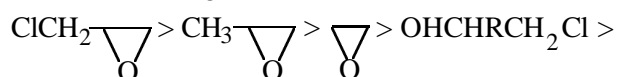
To prepare more efficient catalytic systems for carbonylation of aryl halides, dicobalt octacarbonyl was modified.

Since aryl halides are activated by strongly nucleophilic anionic cobalt complexes, we examined catalytic systems generating new reactive intermediate anionic cobalt complexes.

It is known [10] that $\text{Co}(\text{CO})_4^-$ in alcoholic solutions containing a base undergoes nucleophilic attack of epoxides to form immediately anionic alkylcobalt carbonyl complexes in which the negative charge is localized on the alkyl group. We suggest that catalytic properties of these complexes will differ from those of the anionic complexes formed with alkyl halides after attack of methylate anion on the carbonyl group of the neutral alkylcobalt carbonyl complex. Indeed, as seen from the figure, the cobalt carbonyl–olefin oxide system is more active by a factor of approximately 2 than our most active alkylcobalt carbonyl catalytic system containing benzyl chloride [7–9]. Based on these results, we developed a series of highly active catalytic systems [8, 11, 12] containing olefin oxides, epichlorohydrin, and ethylenechlorohydrin as cocatalysts (see figure). All these cocatalysts, as well as epoxides, form intermediate anionic complexes, with epichlorohydrin being more active owing to the presence of two functional groups. These cocatalysts are not consumed by the parallel pathway of self-carbonylation (as does benzyl chloride). These compounds may undergo methanolysis but this reaction is insignificant in the presence of weak bases such as alkali metal carbonates. The methanolysis products, monomethyl ethers of glycols can be readily separated from the target products, arylcarboxylic acids.

An important advantage of epoxide cocatalysts is the absence of halogen atom in their composition. Hence, the base is not consumed for binding the halogen. Propylene oxide is the most available, cheap, and convenient in use.

The activity of the examined cocatalysts decreases in the following order:



Conversion β of α -chloronaphthalene in the presence of different cocatalysts: (1) $\text{ClCH}_2\text{COOCH}_3$, (2) PhCH_2Cl (dashed line reflects the reaction course after introduction of additional portion of benzyl chloride), (3) $\text{C}_8\text{H}_{17}\text{Br}$, (4) $\text{ClCH}_2\text{CH}_2\text{OH}$, and (5) $\text{CH}_3\text{CH}(\text{O})\text{CH}_2$ as a function of time τ . $T = 60^\circ\text{C}$, $P_{\text{CO}} = 1 \text{ atm}$, $[\text{Co}_2(\text{CO})_8] = 0.017 \text{ M}$.

The mechanism of carbonylation of aryl halides in the presence of $\text{Co}_2(\text{CO})_8$ –epoxide catalytic system is similar to that of the reaction catalyzed by cobalt carbonyl modified with benzyl chloride [4, 8]. The mechanism of carbonylation of aryl halides in the presence of cobalt carbonyl–epoxide–base catalytic system can be described by a catalytic cycle (see scheme).

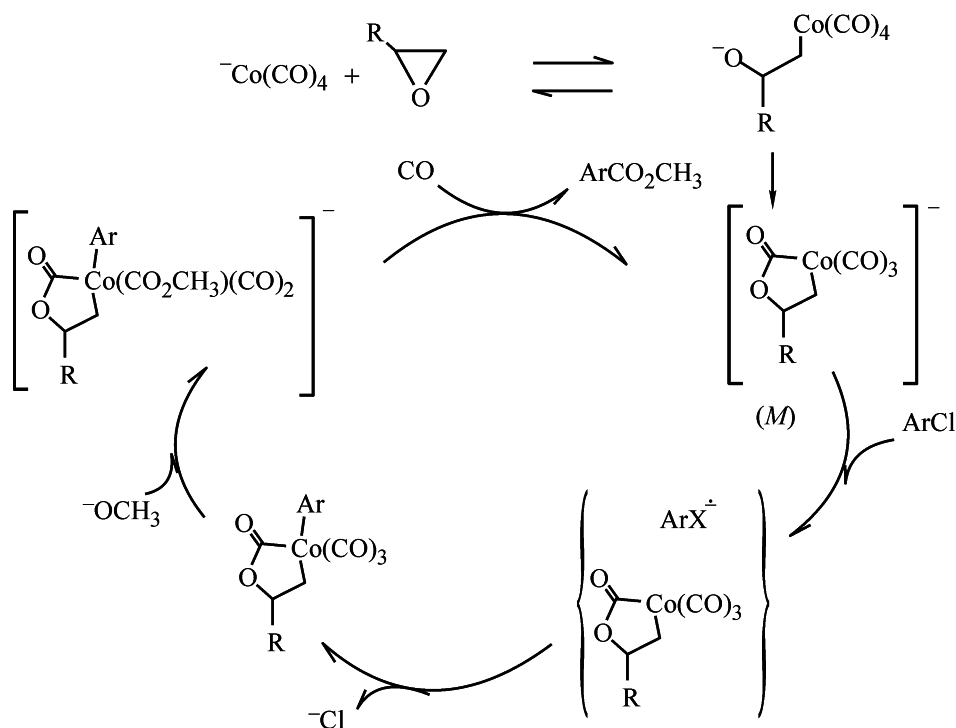
In this system, $\text{Co}(\text{CO})_4^-$ anion reacts with epoxide with opening of the three-membered epoxy ring to form intermediate anionic complex. Probably, this complex is subjected to cyclization into negatively charged metallalactone M which is a “true” catalyst of aryl halide carbonylation.

This complex is highly nucleophilic and activates ArHal by the $S_{\text{RN}}1$ mechanism (which is confirmed by the fact that this reaction is inhibited by aromatic nitro compounds and other one-electron acceptors) via formation of arylalkylcobalt carbonyl complex. Formation of metallalactones from metal carbonyls has been demonstrated with an example of alkylcobalt carbonyl complexes of iron [13].

The main examples of highly efficient synthesis of mono- and polyaromatic acids performed for the first time by carbonylation of the corresponding aryl halides in methanol in the presence of $\text{Co}(\text{CO})_4^-$ –propylene oxide– K_2CO_3 catalytic system are presented in Tables 1 and 2.

As seen from Tables 1 and 2, $\text{Co}(\text{CO})_4^-$ –propylene oxide– K_2CO_3 catalytic system can be used for selective synthesis of aromatic mono- and dicarboxylic acids in a high yield in methanol under very mild

Catalytic cycle of ArHal carbonylation



conditions. This method is suitable for both laboratory preparation and industrial production of aromatic carboxylic acids. It should be noted that a large amount of the activator (epoxide) should be used to prepare the target product in a high yield. This is due to con-

sumption of the epoxide by its methanolysis with the solvent in the presence of a weak base. However, this fact does not minimize the importance of both the laboratory and industrial procedures. Methanolysis of propylene oxide and ethylene oxide (more convenient

Table 1. Carbonylation of aryl monohalides

Run no. ^a	Aryl halide	Molar ratio ^b	Reaction time, h	Aryl halide conversion, ^c %	Yield, ^d %
1	PhBr	30 : 1 : 30 : 90	6.0	89	82 (92)
2	<i>p</i> -FC ₆ H ₄ Br	50 : 1 : 40 : 120	6.0	94	89 (95)
3	<i>o</i> -CF ₃ C ₆ H ₄ Br	133 : 80 : 311	8.0	98	92 (94)
4	<i>m</i> -CF ₃ C ₆ H ₄ Br	123 : 1 : 86 : 307	7.0	100	96 (96)
5	<i>p</i> -BuC ₆ H ₄ Br	15 : 1 : 30 : 40	3.5	83	80 (96)
6	4-F-2-CH ₃ C ₆ H ₃ Br	143 : 1 : 106 : 394	10.0	60	58 (97)
7	<i>p</i> -(cyclo-C ₆ H ₁₁)C ₆ H ₄ Br	20 : 1 : 40 : 60	4.0	90	87 (97)
8	α -C ₁₀ H ₇ Cl	25 : 1 : 20 : 70	2.5	96	92 (96)
9	6-MeO-2-Br-C ₁₀ H ₆	67 : 1 : 100 : 220	10.5	100	100 (100)
10	5-Br-acenaphthene	130 : 1 : 157 : 260	6.0	70	50 (71) ^e
11	<i>p</i> -CH ₃ COC ₆ H ₄ Br	290 : 1 : 153 : 447	6.0	78	74 (95)
12	4-MeO-3-BrC ₆ H ₃ CHO	81 : 1 : 67 : 193	9.0	95	80 (84)
13	4-BnO-3-BrC ₆ H ₃ CHO	97 : 1 : 104 : 245	10.0	74	64 (86)
14	2-EtO-5-BrC ₆ H ₃ CHO	43 : 1 : 50 : 104	9.0	26	20 (77)

^a $T = 60^\circ\text{C}$, $P_{\text{CO}} = 1 \text{ atm}$, $[\text{Co}_2(\text{CO})_8] = 2.7 \text{ g l}^{-1}$ (0.008 mol). ^b Aryl halide : cobalt carbonyl : propylene oxide : potassium carbonate molar ratio. ^c Determined by GLC. ^d Preparative yield of the corresponding arenecarboxylic acid (in parentheses, the yield determined taking into account isolated unchanged aryl halide). ^e Unchanged aryl halide recovered from the reaction mixture contains 25% acenaphthene formed by reduction of the initial 5-bromoacenaphthene (9% of the initial aryl halide).

Table 2. Carbonylation of aryl dihalides

Run no. ^a	Aryl halide	Molar ratio ^b	Reaction time, h	Aryl halide conversion, ^c %	Content of dicarboxylic acid in the reaction product, ^d %
1		41 : 1 : 20 : 125	7.0	99	95
2		50 : 1 : 50 : 220	7.0	94	94
3		35 : 1 : 30 : 100	4.0	81	87
4		24 : 1 : 30 : 90	4.0	99	93
5		10 : 1 : 20 : 60	4.5	96	82

^a $T = 60^\circ\text{C}$, $P_{\text{CO}} = 1 \text{ atm}$, $[\text{Co}_2(\text{CO})_8] = 2.7 \text{ g l}^{-1}$ (0.008 mol). ^b Aryl halide : cobalt carbonyl : propylene oxide : potassium carbonate molar ratio. ^c Determined by GLC. ^d Reaction mixture contained not only dicarboxylic acids but also the corresponding monohaloarene-carboxylic acids. Base is KOH.

for industrial purposes) yields monomethyl ether of propylene glycol and methyl Cellosolve, respectively. These compounds are quite compatible as solvents with methanol and can be readily separated from the aromatic carboxylic acid (the main reaction product). If necessary, they can be recovered separately in the step of methanol regeneration.

A number of aromatic carboxylic acids were successfully prepared from the corresponding aryl halides by this procedure in a 100-l pilot reactor. This method was also tested for dechlorination of environmentally hazardous highly heat-resistant dielectrics prepared from polychlorobiphenyls (PCB). These compounds belong to the family of dioxin-like stable organic pollutants. For this purpose, we tested the new catalytic systems. Previously we found that the least reactive aryl chlorides, chlorobenzene, chlorodiphenyl, and 4,4'-dichlorodiphenyl, are not carbonylated. At the same time, model PCB (congeners) containing 3–4 chlorine atoms are carbonylated under these conditions to form various polychlorobiphenylcarboxylic acids (Table 3).

We found that from 1 to 4 halogen atoms can be involved in the carbonylation. Carbonylation of individual PCBs is a new procedure for preparing a

series of polyaromatic and polyhaloaromatic carboxylic acids which can be used for both laboratory synthesis and industrial production of a number of unique chemical products for preparing new (e.g., electroluminescent) materials. It should be noted that many of these compounds were prepared for the first time by the above procedure. Thus, we proposed a new procedure for processing PCBs under mild conditions in the presence of available catalytic systems [14].

EXPERIMENTAL

Carbonylation was performed in laboratory temperature-controlled glass reactors in a CO flow under vigorous stirring at atmospheric pressure. The reaction products were analyzed by GLC and ^1H NMR spectroscopy. The products were identified by NMR (PFG, DQF ^1H , ^1H COSY; PFG ^1H , ^{13}C HMQC; PFG ^1H , ^{13}C HMBC) spectroscopy and mass spectrometry.

CONCLUSIONS

(1) A new procedure was developed for preparing aromatic and heteroaromatic carboxylic acids and their

Table 3. Carbonylation products of individual PCBs

Initial PCB	Reaction products
	 9 : 1

derivatives (esters and salts) by carbonylation of the corresponding aryl halides in the presence of new catalytic systems containing cobalt carbonyl modified with epoxides.

(2) Carbonylation occurs in a high yield and with a high selectivity under mild conditions (CO pressure of 1–3 atm) in alcoholic solutions containing a base.

(3) A series of mono- and dicarboxylic aromatic acids were prepared for the first time by this procedure.

REFERENCES

- Sheldon, R.A., *Chemicals from Synthesis Gas: Catalytic Reactions of CO and H₂*, Dordrecht: Reidel, 1983. Translated under the title *Khimicheskie produkty na osnove sintez-gasa*, Moscow: Khimiya, 1987, pp. 111–120.
- Zhesko, T.E., Shygalevsky, V.A., and Novikova, E.G., *Fundamental Research in Homogeneous Catalysis*, New York: Gordon and Breach, 1986, vol. 3, pp. 1141–1152.
- Magerlein, W., Indolese, A., and Beller, M., *J. Organomet. Chem.*, 2002, vol. 641, pp. 30–40.
- Zhestko, T.E., Boyarskii, V.P., Nikitina, A.G., and Novikova, E.G., *Protsessy neftepererabotki i neftekhimii* (Processes of Oil Refining and Petrochemistry), Moscow: TNITNeftekhim, 1989, vol. 1, pp. 121–132.
- RF Patent 2047592.
- Foa, M. and Francalanci, F., *J. Mol. Catal.*, 1987, vol. 41, nos. 1–2, pp. 89–107.
- Zhesko, T.E., Boyarskii, V.P., and Beletskaya, I.P., *Metalloorg. Khim.*, 1989, vol. 2, no. 2, pp. 385–387.
- Zhesko, T.E., Boyarskii, V.P., and Nikitina, A.G., *Zh. Obshch. Khim.*, 1998, vol. 68, no. 1, pp. 85–89.
- RF Patent 1825488.
- Organic Synthesis via Metal Carbonyls*, Wender, I. and Pino, P., Eds., New York: Interscience, 1968, vol. 1. Translated under the title *Organicheski sintez cherez karbonily metallov*, Nesmeyanov, A.N., Ed., Moscow: Mir, 1970, p. 296.
- Zhesko, T.E. and Boyarskii, V.P., *Kinet. Katal.*, 1994, vol. 35, no. 2, p. 320.
- RF Patent 2064921.
- Carbon, P. and Sellin, M., *Organometallics*, 2002, vol. 21, no. 11, pp. 2196–2202.
- RF Patent 2215729.