Preparation of Phthalates via Carbonylation of *o*-Dibromobenzenes in Solutions of Pd Catalysts and Reactivity of Ar–Br Bonds

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Abstract—Carbonylation of *o*-dibromobenzene and its derivatives in the presence of palladium phosphine complexes with NaOAc or Et_3N additive leads to the formation of phthalates in high yield under mild conditions. Correlation NMR spectroscopy data and semiempirical calculations have shown that the reactivity of the C–Br bond is enhanced with the increase in the positive charge at the carbon atom, in line with the results of kinetic experiments.

Keywords: carbonylation, *o*-dibromobenzene derivatives, palladium complex, Ar–Br bond reactivity **DOI:** 10.1134/S1070363217100048

Aromatic polycarboxylic acids and their esters are widely applied as monomers for the production of thermostable fibers, liquid-crystalline polymers, protective coatings, dyes, plasticizers, and repellents as well as in the synthesis of medicines and other valuable products [1]. Furthermore, phthalic acid esters in the synthesis of medicinal preparations of phthalocyanine (Pc) structures used for photodynamic therapy and diagnostics of tumors [2], promising ¹³C-labeled substances for various diagnostic issues [3] including diagnostics of tumors by means of ¹³C NMR (Scheme 1) are being developed.



Liquid-phase catalytic carbonylation of aryl halide via the $ArX_2 + 2CO + 2ROH = Ar(COOR)_2 + 2HX$ reaction (X being a halogen, R = H or Alk) is among the most promising approaches to the preparation of phthalates and other derivatives of aromatic acids. In contrast to conventional methods of alkylaromatic compounds oxidation [4], the mentioned method exhibits several important advantages such as high yield and selectivity with respect to the target product, relatively mild conditions, and high reaction rate. However, the available reference data have mainly addressed processes of carbonylation of aryl monohalides (Ar–X) leading to benzoic acid and its derivatives [5].

The data on the synthesis of aromatic polycarboxylic acids via carbonylation of aromatic polyhalides as well as on the effects of the substituents on the reactivity of the C–X bonds have been fairly scarce. For example, carbonylation of 1,2- and 1,4-diiodobenzenes in solutions of Pd(OAc)₂ leads to phthalic and terephthalic acids [6]. 1,8-Diiodonaphthalene can be converted into diamides of 1,8-naphthalenedicarboxylic acid in the presence of the Pd(OAc)₂–PPh₃– R₂NH catalytic system [7]. The reaction of substituted 2,4-dibromobenzophenone under CO atmosphere have afforded diesters in 92% yield, the highest activity being observed in the cases of catalytic systems based



on PdCl₂-dppf [dppf = 1,1'-bis(diphenylphosphino)ferrocene] [8].

Reactivity of various dichloropyridines in the presence of Pd-phosphine systems and bases (NaOAc and Et₃N) has been demonstrated in [9–11]. For example, 5-methoxymethyl-2,3-dichloropyridine in the presence of the Pd(OAc)₂–dppf–NaOAc system (146°C, 15 atm CO) has been converted in the diester with selectivity 99% and yield 90% [11]. The complexes with dppf have been found more active than these with 1,1'-bis(diphenylphosphino)butane (dppb) and other diphosphines, and the nature of the substituent in the aromatic ring [5-MeOCH₂ or 5-MeOC(O)] practically does not affect the product yield.

The effect of the substituent on carbonylation of substituted bromobenzenes affording butyl benzoates has been shown in Ref. [12]: the yield of the ester in the presence of the Pd(OAc)₂–dtbpx–Cs₂CO₃ system [dtbpx = bis(di-*tert*-butylphosphino)-*o*-xylene] (80°C, 2.8 atm CO) has ranged between 36 and 95%; the acceptor substituents in the *para*-position with respect to bromine activate the substrate as compared to the donor ones, whereas the acceptors in the *ortho*-position reduces the reactivity by 15%.

Peculiar data on the discussed matter have been recently published [13, 14]. Ionic liquids noticeably activate the Pd catalyst in carbonylation of substituted bromobenzenes, and allow to reduce CO pressure to 1 atm [15, 16] and to reach high yields of benzoates (90–95%).

It has been stated that the activation of aryl halides ArX by Pd(0) complexes in the carbonylation reactions [14] occurs via the nucleophilic substitution mechanism [17, 18]. The anionic complex $L_2Pd^0X^-$ (X = Hlg or OAc) is the active form of the Pd(0) complex (nucleophile), as confirmed by the data on the increase in the catalyst activity by ionic liquids forming the [L_2Pd^0X]⁻[NR₄]⁺ species [16]. Furthermore, it has been shown that the oxidative addition (activation) of aryl halides to complexes of nickel and cobalt occurs via the nucleophilic attack of the Ar–X bond by anionic complexes L_nMX^- of these metals [19–21]. The ease of the nucleophilic attack of the Pd

complex at the C–Br bond of the heteroaromatic ring explains also the high yield of the products of aminocarbonylation of 4,5-dibromo-2-methylpyridazin-3(2*H*)one [22].

Yet, in our point of view, the available reference data are not sufficient for wide practical application of carbonylation of aromatic polyhalides to obtain aromatic polycarboxylic acids and their derivatives. Moreover, the development of efficient synthesis of substituted phthalic esters labeled with the ¹³C isotope [for example, $RC_6H_3(^{13}COOMe)_2$] and further preparation of ¹³C_n-phthalocyanines for medical diagnostics started in our earlier studies [2, 3] is of practical importance. This work hence aimed to elucidate the substituent effects on the reactivity of aromatic bromine atoms using the example of liquid-phase carbonylation of o-dibromobenzene and its tert-butyl derivative and to clarify the nature of the activation of the C-Br bonds in that substrate by the catalysts based on palladium complexes.

In the preliminary experiments, we elaborated the conditions of carbonylation of aryl dibromides using *o*-dibromobenzene as the example. The reaction was performed in methanol in the presence of the $Pd(OAc)_2$ – PPh_3 or $Pd(OAc)_2$ –dppf catalytic systems; triethylamine or sodium acetate was used as the additive. Chromato–mass spectrometry (GC/MS) analysis of the reaction mixture revealed that the reaction gave dimethyl phthalate, methyl 2-bromobenzoate being the intermediate (Scheme 2).

The results of the elaboration of the reaction conditions are collected in the table. It was found that the Pd(OAc)₂–PPh₃–NaOAc catalytic system exhibited good activity (exp. 1) only under severe conditions (150°C, $p_{CO} = 60$ atm): reduction of the pressure resulted in the decrease in the yield of dimethyl phthalate (from 100 to 65.2%, exp. 3), despite the increase in the concentration of *o*-dibromobenzene. The exchange of PPh₃ with dppf significantly enhanced the activity of the catalytic system and allowed using milder conditions: for example, other conditions being the same (exp. 3 and 9), the change of the ligand led to the increase of dimethyl phthalate fraction in the products mixture by almost 30% (to

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Exp. no.	p, ^a atm	t, °C	τ, h	Concentration, mol/L \cdot 10 ²				Conversion	Content in the products, %		
				<i>o</i> -dibromo- benzene	Pd ^b	L	additive	of <i>o</i> -dibromo- benzene, %	<i>o</i> -dibro- mobenzene	monoester	dimethyl phthalate
PPh ₃ -NaOAc											
1	60	150	9.5	9.8	1.1	10.6	29.8	100.0	0	0	100.0
2	60	150	9.25	2.8	1.0	10.4	86.5	90.1	8.3	11.6	80.1
3	5	150	8.0	28.8	1.2	11.9	64.8	88.9	16.5	18.3	65.2
PPh ₃ -Et ₃ N											
4	60	150	8.0	25.7	0.9	9.2	77.2	100.0	0	0	100.0
5	5	150	8.0	25.7	0.9	9.1	77.2	100.0	0	3.6	96.4
6	5	130	8.0	26.4	0.9	9.4	60.3	100.0	0	0	100.0
7	3	130	5.67	26.4	0.9	9.4	60.3	68.1	32.9	24.7	42.3
8	1	130	4.83	26.4	1.6	13.6	60.3	0	100.0	0	0
dppf–NaOAc											
9	5	150	9.0	28.8	1.5	0.9	60.9	95.1	5.6	0	94.4
10	2	100	7.25	28.8	1.7	0.9	60.5	80.4	18.9	11.4	69.7
11	2	100	5.0	28.8	1.7	1.8	62.6	91.4	10.0	6.7	83.3
dppf–Et ₃ N											
12	2	100	1.33	26.4	1.5	1.9	60.3	98.3	1.8	1.0	97.3
13	1	100	4.33	26.4	1.5	1.6	60.3	99.1	1.0	4.3	94.7
14	0	100	0.67	26.4	1.5	1.7	60.3	73.2	31.7	12.4	55.9
15	1	100	1.08	26.4	2.7	3.1	60.3	99.9	0.2	0.6	99.3
16	2.5	100	1.58	24.7	2.2	2.0	54.5	99.8	0.2	0	99.8

Carbonylation of 1,2-dibromobenzene in dimethyl phthalate in the presence of Pd(OAc)₂

^a Excess pressure (in Exp. 14, absolute pressure of CO was 1 atm). ^b Pd(OAc)₂.

above 94%), and even upon further decrease in the pressure and temperature (to 2 atm and 100°C, exp. 10 and 11) the fraction of dimethyl phthalate still exceeded 83%, the amount of dppf being much lower than in the case of PPh_3 (cf. exp. 3). The advantages of the use of dppf were more clear in comparison of exp. 8 (the reaction did not occur) and 13 (dimethyl phthalate fraction in the products was close to 95%). Furthermore, triethylamine use as the base was advantageous over sodium acetate. For example, the $Pd(OAc)_2$ -dppf-Et₃N, 1 : 1 : 20 system (exp. 15) allowed quantitative yield of dimethyl phthalate at 100°C and p_{CO} 1 atm (excess) within 1 h. At the same time, the catalyst turnover frequency under mild conditions {TOF = $[o-dibromobenzene]/([Pd]*\tau)$ } was increased approximately tenfold (exp. 1 and 15).

It should be noted that the selectivity of the process could be enhanced (i.e. the fraction of the monoester in the products mixture could be decreased) with the increase in the dppf/Pd ratio and the CO pressure. For example, the increase in the dppf/Pd ratio from 0.5 : 1 to 1 : 1 led to the decrease in the monoester fraction in the products mixture from 11.4 to 6.7% (exp. 10 and 11), whereas the increase in p_{CO} from 1 to 3.5 atm (abs.) resulted in the decrease in the monoester fraction from 12.4 to 0% (exp. 14–16).

The conditions elaborated for carbonylation of *o*dibromobenzene were further used in the study of reactivity of Br atoms in 4-*tert*-butyl-1,2-dibromobenzene. At the 4-*tert*-butyl-1,2-dibromobenzene : $Pd(OAc)_2$: dppf : Et₃N ratio of 39 : 1 : 1 : 83 in the





methanolic solution (100°C, $p_{CO} = 3$ atm), the yield of dimethyl 4-*tert*-butylphthalate was 98%. The GC/MS analysis of the reaction mixture corresponding to the incomplete process revealed that the reaction intermediates were methyl esters of 2-bromobenzoic acids with a *tert*-butyl substituent in the aromatic ring, m/z: 270, 272 $[M]^+$; 255, 257 $[M - CH_3]^+$; 239, 241 $[M - OCH_3]^+$; 227, $[M - C_3H_7]^+$. The presence of a strong σ -donor substituent in the starting dibromobenzene led to the non-equivalence of the C–Br bond, and the ratio of the concentrations of the intermediate monoesters was at least 5 : 1.

However, the obtained mass spectra did not allow reliable elucidation of the position of *tert*-butyl group in the aromatic ring of the intermediate monoesters; therefore, their structures were determined by means of correlation NMR spectroscopy of the reaction products labeled with ¹³C (Scheme 3).

The NMR analysis allowed unambiguous assignment of the three aromatic protons of each of the reaction mixture components. The ¹H-¹H COSY spectrum contained the signals of spin-spin interaction of the protons of the t-Bu group with the adjacent protons (o-H) of the aromatic ring. The heteronuclear ¹H–¹³C HMBC spectrum contained the signals of the spin-spin interaction of the protons (o-H) of the aromatic ring with the ¹³C atoms of the ¹³COOMe group. Since the spectra contained the signals of only one of the two monoesters (the major one), we concluded that it was the major monoester that contained the aromatic proton interacting with both tert-butyl and the ester groups (i.e. positioned between them). Hence, the major intermediate was identified as methyl 5-tertbutyl-2-bromobenzoate, the product of substitution of Br atom in the *meta*-position with respect to the *tert*butyl group of 4-tert-butyl-1,2-dibromobenzene.

Elucidation of the structure of intermediate monoesters allowed the study of the reactivity of the C–Br bonds in the *ortho-* and *para*-positions with respect to the *tert*-butyl group of the starting 4-*tert*-butyl-1,2dibromobenzene. To do so, we performed the kinetic experiments and determined the rate constants of the formation of the intermediate and the final products. Kinetics of carbonylation of 4-*tert*-butyl-1,2-dibromobenzene was studied under the following conditions: 100° C, p_{CO} 2 atm, [Pd(OAc)₂] = 7×10^{-3} mol/L, 4-*tert*butyl-1,2-dibromobenzene : Pd(OAc)₂ : dppf : Et₃N = 46 : 1 : 1 : 98, methanol as solvent. Typical kinetic curves are shown in Fig. 1.

The obtained kinetic curves of carbonylation of 4*tert*-butyl-1,2-dibromobenzene (Fig. 1a) revealed the shape typical of the serial-parallel processes, and the consumption of the starting dibromide followed the first-order reaction kinetics (Fig. 1b) up to high conversion (disregarding the short induction period). The convergence of the material balance throughout the process evidenced no formation of the nonidentified side products.

Basing on the obtained data and assuming the firstorder kinetics of consumption of the intermediate monoesters as well as stationary conditions for the concentration of the dissolved palladium complex, we derived the kinetic model of the liquid-phase catalytic carbonylation of 4-*tert*-butyl-1,2-dibromobenzene (Scheme 4).

The values of the reaction rate constants obtained via optimization of the parameters for the kinetic model were as follows: $k_1 (3.8\pm0.4)\times10^{-3}$, $k_2 (0.8\pm0.4)\times$ 10^{-3} , $k_3 (5.5\pm0.8)\times10^{-3}$, and $k_4 (21.8\pm16.0)\times10^{-3}$ min⁻¹. The built model described well the experimental data (see Fig. 1). The rate constants ratio $k_1/k_2 = 4.6$ stages of the monoesters formation evidenced the significantly higher reactivity of the C–Br bond in the *meta*position with respect to the *tert*-butyl group than the *para*-bond, that fact likely being related to the localization of the positive charge at the *meta*-carbon atom of 4-*tert*-butyl-1,2-dibromobenzene caused by



Fig. 1. Kinetics of carbonylation of 4-*tert*-butyl-1,2-dibromobenzene in methanol (a) and determination of the reaction order with respect to 4-*tert*-butyl-1,2-dibromobenzene (b). $[Pd(OAc)_2] = 7 \times 10^{-3} \text{ mol/L}$, 4-*tert*-butyl-1,2-dibromobenzene–Pd(OAc)₂–dppf–Et₃N = 46 : 1 : 1 : 98, 100°C, $p_{CO} = 2$ atm; (1) 4-*tert*-butyl-1,2-dibromobenzene, (2) dimethyl phthalate, (3) *meta*-ester, (4) *para*-ester; (points) experiment, (lines) calculation using Scheme 4.

the +*I*-effect of the *t*-Bu group. Moreover, the k_4/k_3 value 4.0 for the stages of consumption of the monoesters confirmed the enhancement of the reactivity of the *meta* C–Br bond due to the additional acceptor effect of the COOMe group in the *para*-ester (Scheme 3).

To verify the suggested increase in the positive charge at the carbon atoms of the C–Br bonds in the *meta*-position with respect to the *t*-Bu group of 4-*tert*-butyl-1,2-dibromobenzene and the monoesters, we calculated the partial charge using the CNDO method with geometry optimization.

The obtained data revealed that the positive charge at the aromatic C atoms of the C–Br bonds in the *meta*position with respect to the *tert*-butyl group of 4-*tert*butyl-1,2-dibromobenzene was significantly higher than that in the *para*-position, facilitating the nucleophilic attack of the *meta*-bond Ar–Br with the active Pd complex at the stage of the oxidative addition; the same was held for the isomeric monoesters. The values of the charge were well correlated with the rate constants of carbonylation at the C–Br bonds determined earlier: the Br atom in the *para*-position with respect to the *t*-Bu group of 4-*tert*-butyl-1,2-dibromobenzene was the least reactive (k_2), and the atom in the *meta*-position with respect to the *t*-Bu group of methyl 4-*tert*-butyl-2bromobenzoate was the most reactive (k_4). Those data confirmed the suggestion of the activation of aryl halides with the Pd complexes in the reactions of carbonylation via nucleophilic substitution mechanism.



Basing on the performed study, we elaborated an efficient method of the synthesis of dimethyl 4-*tert*-butyl[2,2'-¹³C₂-carbonyl]phthalate [23] (Scheme 3) with the degree of isotopic enrichment 99% (¹³C NMR data)



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for the preparation of promising phthalocyanine drugs used in the tumor diagnostics [2, 3].

In summary, it was found that the synthesis of phthalic acid derivatives via carbonylation of aryl dibromides in solutions of Pd complexes could occur under mild conditions ($80-100^{\circ}$ C, 1-3 atm CO) with high yield of the target products (at least 98%). As exemplified by the *tert*-butyl-substituted *o*-dibromobenzene, the carbonylation reaction was accelerated with the increase in the positive charge at the carbon atoms of the C–Br bond. The obtained data allowed prediction of the outcome of carbonylation of aryl dibromides to optimize the synthesis of target derivatives of aromatic polycarboxylic acids under mild conditions with high yield.

EXPERIMENTAL

Quantitative analysis was performed using a Kristallyuks-4000M gas chromatograph (flame ionization detector, SE-54 phase, column 15 m × 0.32 mm, 2-meth-oxyacetophenone as the internal standard). Chromatomass spectrometry analysis was performed using an Agilent 6890N instrument (mass detector 5975, column HP-5MS 30 m × 0.25 mm, EI, 70 eV). The NMR correlation spectroscopy experiments ${}^{1}\text{H}{-}^{1}\text{H}$ COSY and ${}^{1}\text{H}{-}^{13}\text{C}$ HMBC were performed using a Varian Unity Inova 500M instrument (DMSO- d_6 99.8% as solvent, TMS as reference). The partial charge at the atoms of the substrates was calculated using the CNDO method (HyperChem 8.0.3 software) with optimization of the molecule geometry via the Polak–Ribiere method [24].

The reactions were performed in a glass reactor immersed in a steel autoclave to prevent contact the autoclave material with the reaction mixture [25]. When ¹³CO was used, it was fed from a small container weighed with accuracy 0.01 g; after the reaction was complete, the residual labeled gas was collected in another container for further use and calculation of the material balance. ¹³CO was obtained via reduction of ¹³CO₂ (isotopic purity 99 mol%) as described elsewhere [26].

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butyl-1,2-dibromobenzene.

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