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Pd(OAc)$_2$-catalyzed oxidative carbonylation of aromatics: synthesis of naphthalenecarboxylic acids

Alexander R. Elman *

Rostkhim Ltd, 38, Shosse Entuziastov, 111123 Moscow, Russia

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ABSTRACT

The liquid-phase oxidative carbonylation of aromatics leading to aromatic carboxylic acids is studied to develop new approaches to 2,6-naphthalenedicarboxylic acid (NDA) preparation. It is shown that the catalytic system Pd(OAc)$_2$/$K_2S_2O_8$ allows the synthesis of naphthalic anhydride (NAn) by direct oxidative carbonylation of naphthalene under mild conditions (25 °C, 2 atm CO). The subsequent alkaline hydrolysis of NAn and isomerization of the obtained 1,8-naphthalenedicarboxylic acid salt is known to lead to NDA.

Aromatic carboxylic (including, polycarboxylic) acids are used widely for the production of medicines, monomers, and dyes.[1] 2,6-Naphthalenedicarboxylic acid (NDA) is very important among aromatic acids because it is used in the production of polyethylene naphthalate polymers, and other polyamides, polyesters, and polyamides.[2] Traditional production of aromatic acids is, as a rule, multistage, and is based on the oxidation of alkyl aromatics, however the low selectivity of this process reduces considerably the economic efficiency. On the other hand, oxidative carbonylation allows aromatic acids to be obtained in one or two steps using cheap aromatic hydrocarbons, with high selectivity under mild conditions[1,3] and therefore is very promising for the production of the desired products.

For the synthesis of aromatic carboxylic acids under mild conditions catalytic systems based on Pd(OAc)$_2$ are used.[1] Benzoic acid was obtained from benzene in 100% yield under mild conditions (1 atm, 20 °C) in a CO atmosphere when $K_2S_2O_8$ was used as the oxidizing agent.[4] The selectivity of 2-naphthoic acid formation from naphthalene reaches 92% in the presence of 1,10-phenanthroline (Phen) under the action of a CO/O_2-mixture.[5] It is known that 2-naphthoic acid potassium salt, at elevated temperature, is transformed into the salt of 2,6-naphthalenedicarboxylic acid in high yield (90%).[6] Under similar conditions the potassium salt of 1,8-naphthalenedicarboxylic acid isomerizes into the salt of NDA in a yield of 70%.[7] In the present work, the possibility of a one-step synthesis of naphthalic anhydride is described by the way of naphthalene oxidative carbonylation under mild conditions (20 °C, 2 atm). In turn, naphthalic anhydride can be converted into NDA through intermediate formation of 1,8-naphthalenedicarboxylic acid.[8]

Oxidative carbonylation of benzene

The oxidative carbonylation was carried out as described earlier[9] under the following conditions: [Pd(OAc)$_2$] = 1.7×10^{-2} M; [C_6H_6] = 1.9 M. We added $K_2S_2O_8$ 10 mmol and 10 mL of solvent—TFA. The temperature was 22 °C and the CO pressure was 2 atm. The only product of the reaction was benzoic acid, the yield of which reached 13% with respect to benzene in 20 h. Figure 1 shows the change of benzoic acid yield versus time.

Thus, benzoic acid can be obtained by the direct oxidative carbonylation of benzene in a good yield based on the initial

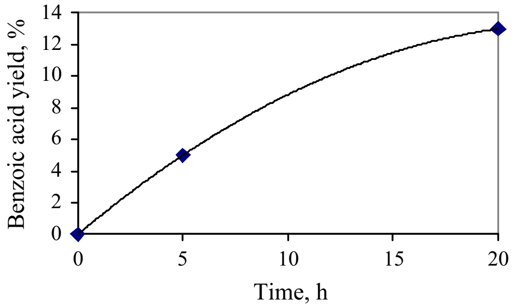

Figure 1. Dependence of benzoic acid yield versus time.

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* Tel.: +7 903 548 7809; fax: +7 495 673 6310.
E-mail address: elmanar@yandex.ru

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hydrocarbon and a very considerable yield (1450%) based on Pd. Thus the Pd catalyst does not lose activity and the formation of Pd^0 was not observed.

In consideration of the high selectivity and mild conditions, this method is of practical interest and deserves further study as it should be extendable to other aromatics, including naphthalene, for the purpose of obtaining naphthoic acids.

Oxidative carbonylation of naphthalene

Preliminary experiments

Data on naphthalenecarboxylic acid synthesis by the oxidative carbonylation of naphthalene in the presence of the $Pd(OAc)_2$/Phen system have been published.[5] However the procedure described did not provide solubility of naphthalene in the chosen solvent (acetic acid/cyclohexane) at room temperature; this made the analysis of the reaction mixture and the taking of samples difficult during our experiments. So the main task of the preliminary experiments was the choice of a suitable solvent and the concentrations of the components in the reaction mixture.

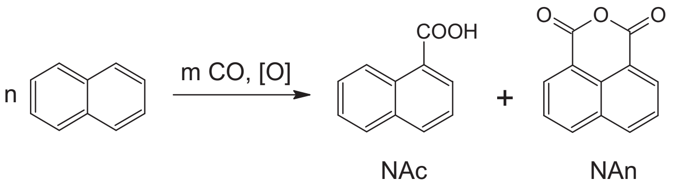
As a result, preliminary experiments were conducted in a solvent consisting of 6 mL of acetic acid and 5 mL of cyclohexane at a temperature of 115 °C; the initial component concentrations were: $[C_{10}H_8] = 1.8$ M; $[Pd(OAc)_2] = 1.9 \times 10^{-2}$ M; $[Phen] = 8.3 \times 10^{-2}$ M. This led to full homogeneity of the reaction mixture both before carrying out the reaction, and after. α-Naphthol and β-naphthol were formed as the products and the results are presented in Table 1 (isomeric naphthols are denoted as α and β).

Table 1 shows that α- and β-naphthols, with preferential formation of α-naphthol, can be obtained under conditions of oxidative carbonylation of naphthalene; no other products were observed. β-Naphthol formation requires the presence of oxygen. The absence of moisture in the solvent has the greatest impact on increasing the catalyst activity. The catalyst is stable and Pd^0 formation does not occur.

Further development of this method is of interest from the point of view of obtaining naphthols directly from naphthalene under mild conditions, since the traditional method includes application of corrosive conditions and is characterized by a large quantity of acid–base waste.[10,11] At the same time, unlike the results reported previously,[5] naphthalenecarboxylic acids were not found in the reaction products.

Naphthalenecarboxylic acid derivatives

Given that benzene, in trifluoroacetic acid under the action of CO in the presence of $Pd(OAc)_2$ and $K_2S_2O_8$, is converted into benzoic acid with high selectivity (Fig. 1), these conditions and catalytic system were used in the subsequent experiments to obtain naphthalenecarboxylic acids by oxidative carbonylation of naphthalene. To conduct the reactions the following conditions were chosen (similar to benzene): $[Pd(OAc)_2] = 2.3 \times 10^{-2}$ M; $[C_{10}H_8] = 1.8$ M; we added $K_2S_2O_8$ (10.6 mmol) and trifluoroacetic acid (10 mL) (solvent); temperature 20 °C and the CO pressure 2 atm.



Scheme 1.

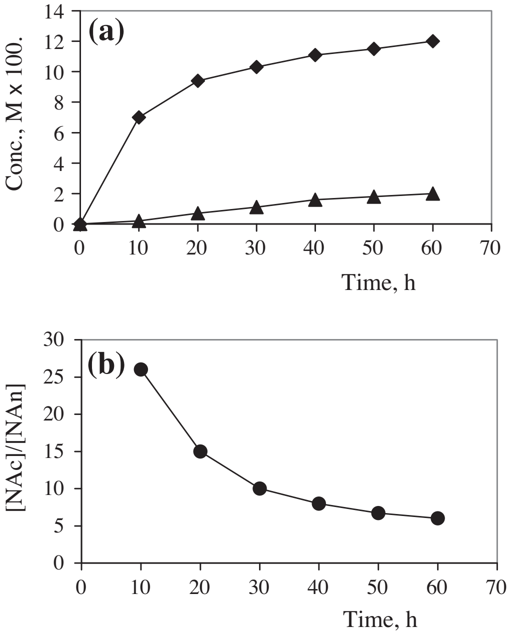


Figure 2. Dependence of (a) the change in 1-naphthoic acid (◆) and 1,8-naphthalic anhydride (▲) concentrations and (b) [NAc]/[NAn] ratio versus time.

The main reaction product (Scheme 1) was 1-naphthoic acid (NAc). Also, for the first time, 1,8-naphthalic anhydride (NAn) was obtained via the oxidative carbonylation of naphthalene. 2-Naphthoic acid formation was not observed in this case.[4]

Figure 2 shows the change in the reaction product concentration and their ratio versus time.

Figure 2 shows that under the chosen conditions the reaction products (1-naphthoic acid and 1,8-naphthalic anhydride) were obtained, probably as a result of consecutive transformations. Thus their total yield reached 7.8% based on initial naphthalene or 608.7% with respect to Pd.

Table 1
Oxidative carbonylation of naphthalene

Run	Time,(h)	Gas composition (atm)	Solvent[a]	Yield[b] of β + α[c] based on Pd, (%)	$[\beta] \times 10^2$ (M)	Ratio β:α
1	25.7	$2\ CO + 2\ O_2$	Without dehydration	50	0.38	1:1.5
2	16.0	$1.4\ CO + 0.7\ O_2$	Water-free	233	0.80	1:3.8
3	16.5	$2\ CO + 1\ O_2$	Water-free	174	1.10	1:2.0
4	19.5	$10\ CO + 1\ O_2$	Water-free	51	0.40	1:1.5
5	17.0	2 CO	Water-free	Traces α	—	—

[a] We used acetic acid after threefold fractional crystallization in water-free solvent.
[b] GLC yield.
[c] α and β denote isomeric α- and β-naphthols.

Choice of reaction conditions and composition of the catalytic system

The influence of the oxidizing agent ($K_2S_2O_8$), the solvent composition, and temperature on the processes leading to 1-naphthoic acid and 1,8-naphthalic anhydride was studied (Table 2).

It is apparent from Table 2 that it is necessary to have a certain molar ratio of an oxidizing agent to $Pd(OAc)_2$ in order to ensure its stability in solution and to prevent metallic palladium formation (runs 1–3).

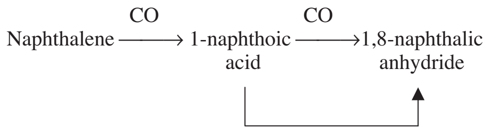
Due to the limited solubility of naphthalene and $K_2S_2O_8$ in the reaction mixture when polar acetic acid was added, the formation of solid particles of naphthalene covered with palladium black was observed (run 5). However under these experimental conditions the addition of cyclohexane (2 mL) led to full solubility of naphthalene and the transition of Pd into solution (product formation was not observed). Thus, potassium persulfate is a re-oxidative agent for palladium under the conditions of oxidative carbonylation. The results of runs 2, 5, and 6 show that it was possible to replace some of the TFA with a less aggressive solvent.

Run 7 shows that in such a complicated heterophase system, even simply increasing the rate of stirring leads to a significant increase in the reaction rate and yield of products: the total yield of products reached 17.5% based on initial naphthalene ([1-naphthoic acid]:[1,8-naphthalic anhydride] = 5.8:1) or 1312% based on Pd. Replacing $K_2S_2O_8$ with Na_2O_2 or oxygen did not lead to success: sodium peroxide decayed considerably with the formation of oxygen under these experimental conditions; also Pd^0 formed, and no products were observed.

Thus, $K_2S_2O_8$ plays an important role, as an effective re-oxidant of palladium which leads to its stability in the reaction mixture, and also probably is the donor of the oxygen which is necessary for product formation (Scheme 1).

Oxidative carbonylation of 1-naphthoic acid

In the previous experiments it was established that during the oxidative carbonylation of naphthalene, 1,8-naphthalic anhydride was formed as a result of consecutive-parallel transformations (see Fig. 1). To clarify how 1,8-naphthalic anhydride was obtained, we carried out several experiments on the oxidative carbonylation of 1-naphthoic acid (Table 3).



Scheme 2.

The results shown in Table 3 show that 1,8-naphthalic anhydride can be obtained by direct carbonylation of 1-naphthoic acid. This confirms the possibility of anhydride formation during the oxidative carbonylation of naphthalene as a result of consecutive reactions through the intermediate formation of 1-naphthoic acid. Hence, the reaction rate, apparently, does not depend on the 1-naphthoic acid initial concentration (runs 1 and 2).

At the same time, in the absence of CO, a small quantity of anhydride was also formed; it should be noted that the reaction proceeds only in the presence of the Pd catalyst under chosen conditions (runs 3 and 4). These results indicate the possibility of 1-naphthoic acid disproportionation with the formation of 1,8-naphthalic anhydride and naphthalene derivatives, which form as a result of C–H bond activation at position 8. They also indicate the participation of these derivatives in a number of other processes (alkylation, cyclization, addition, etc.). 1,8-Naphthalic anhydride formation may occur via consecutive-parallel transformations according to Scheme 2.

Analyses using GC–MS and HPLC showed that in the absence of CO (run 3) the main product of 1-naphthoic acid transformation was 2*H*-naphtho[1,8-*b*,*c*]furan-2-one (**I**), the product of intermolecular cyclization. Besides, the formation of 1,1′-binaphthyl and other products (**II**-**V**) was observed, identified by comparison of their experimental mass spectra obtained during GC–MS analysis of the reaction product mixtures with spectra from the library of

Table 2
Influence of the reaction conditions and catalytic system composition on the results of the oxidative carbonylation of naphthalene

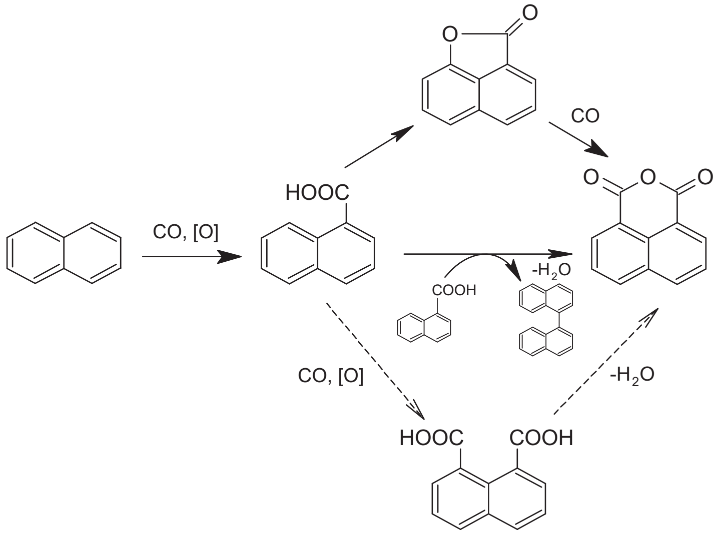
Run	$[Pd(OAc)_2]/[K_2S_2O_8]$, (mol/mol)	Solvent	*T* (°C)	Yield of $\Sigma_{product}$[a] based on $C_{10}H_8$, (%)	Yield of $\Sigma_{product}$[a] based on $K_2S_2O_8$, (%)	Notes
1	1:47.8	TFA	18	7.8	12.7	
2	1:20.0	TFA	25	6.9	28.6	
3	1:10.0	TFA	30	2.8	21.7	Pd^0 formation
4	1:19.6	TFA	30	5.1	20.4	
5[b]	1:21.2	*1st stage:* 2 mL of TFA, 3 mL of AcOH *2nd stage:* 2 mL of cyclohexane added	30	–	–	*1st stage:* Pd^0 formation *2nd stage:* Pd dissolved
6	1:21.5	4 mL of TFA, 1 mL of AcOH	25	6.0	23.0	
7[c]	1:18.4	TFA	25	17.5	71.3	

[a] GLC yield of [1-naphthoic acid] + [1,8-naphthalic anhydride].
[b] The run was continued after cyclohexane (2 mL) addition under the same conditions (see further).
[c] Rate of stirring was increased twice.

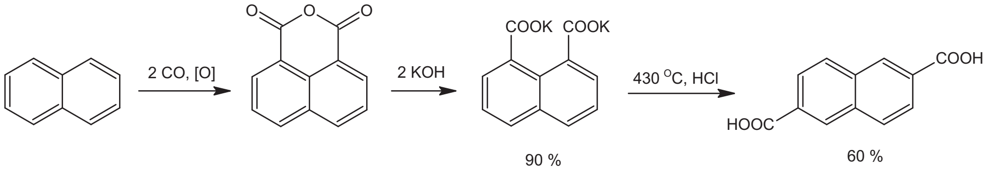
Table 3
Oxidative carbonylation of 1-naphthoic acid

Run	$[Pd]_0 \times 10^2$ (M)	$[K_2S_2O_8]_0$ (M)	$[1\text{-naphthoic acid}]_0$ (M)	Gas	Time (h)	Yield of 1,8-naphthalic anhydride[a], (%)
1	2.25	0.48	1.80	2 atm CO	61.3	12.8
2	2.31	0.45	0.59	2 atm CO	19.5	16.9
3	2.27	0.46	1.81	2 atm N_2	20.3	1.7
4	0	0.45	0.60	2 atm N_2	23.0	–

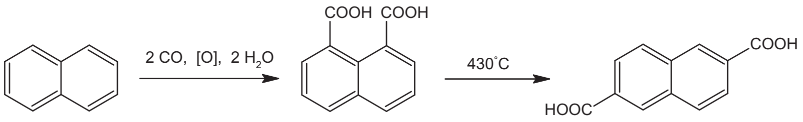
[a] GLC yield based on 1-naphthoic acid.



Scheme 3.

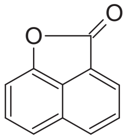


Scheme 4.

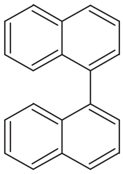


Scheme 5.

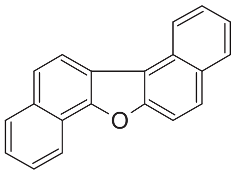
mass spectra.[12] Also, structures **I**–**V** were confirmed by the analysis of electron impact fragmentation of these molecules:



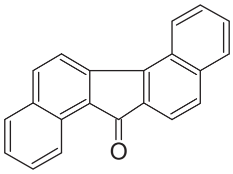
I



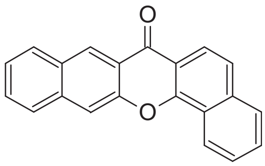
II



III



IV



V

On the other hand, using HPLC, we detected only a small quantity of naphthofuranone (**I**) in the products of 1-naphthoic acid carbonylation (runs 1 and 2). Also, 1,8-naphthalenedicarboxylic acid was formed. The main product of the oxidative carbonylation of 1-naphthoic acid was 1,8-naphthalic anhydride.

The detailed analysis of the products of the transformation of 1-naphthoic acid indicates that oxidative carbonylation of 1-naphthoic acid leads to 1,8-naphthalic anhydride through intermediate formation of 2*H*-naphtho[1,8-*b*,*c*]furan-2-one. 1,8-Naphthalic anhydride can also form as a result of 1,8-naphthalenedicarboxylic acid dehydration. Thus, activation of the C–H bond at position 8 of 1-naphthoic acid and the other C-atoms of naphthalene causes side reactions to occur, including 1-naphthoic acid disproportionation with the formation of the same anhydride and other products (binaphthyl, etc.).

The obtained results allow the following scheme to be proposed for the product formation during the oxidative carbonylation of naphthalene (Scheme 3).

In conclusion, we have shown that oxidative carbonylation of naphthalene leads to naphthalenedicarboxylic acid derivatives via a one-step process under mild conditions. 1-Naphthoic acid is the main reaction product under the chosen conditions, its yield reaches 15% based on the initial naphthalene (total yield of products is 1312% based on Pd; see Table 2). Also, the yield can be increased significantly by improvement of the process conditions (solubility of reagents, temperature, pressure, and probably, prevention of CO oxidation into CO_2), optimization of the catalytic system composition, and other measures.

The important task of this work was the development of possible approaches to 2,6-naphthalenedicarboxylic acid synthesis. From this point of view, the possibility of obtaining 1,8-naphthalic anhydride from naphthalene in one step is very attractive. Under the studied conditions the process proceeds through intermediate 1-naphthoic acid formation; the above-mentioned anhydride, apparently, is the end product of the process.

In the case of the increased yield of 1,8-naphthalic anhydride, a new way of obtaining NDA from naphthalene can be postulated according to Scheme 4, including selective formation of 1,8-naphthalic anhydride, its subsequent hydrolysis, and isomerization of the obtained 1,8-naphthalenedicarboxylic acid salt via a known procedure.[8]

Taking into account that 1,8-naphthalenedicarboxylic acid was found in the reaction products, it could be worth trying to combine the stages of formation and hydrolysis of 1,8-naphthalic anhydride. In this case the process becomes simpler (Scheme 5).

Acknowledgments

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