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# Pd-Catalyzed Selective One-Step Synthesis of β-Naphthoic Acid from Naphthalene and CO

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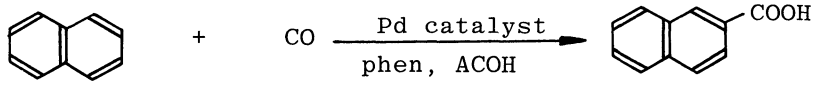
β-Naphthoic acid can be prepared in more than 80% selectivity via one-step carboxylation of naphthalene with carbon monoxide by the Pd/phenanthroline catalyst systems. Pd(0) species such as Pd black are found to be active catalysts as well as $Pd(OAc)_2$. Addition of $O_2$ increases the yield.

We have found that aromatic compounds such as benzene react with olefins to give aromatic-substituted olefins via an Ar-Pd σ-complex intermediate (1) formed by the direct activation of a C-H aromatic bond by the catalysis of Pd(II).[1] 1 has been proved to be an important synthetic intermediate. For example, 1 reacts with arenes,[2] $O_2$ or $H_2O$,[3] and CO[4] or $CO_2$[5] in addition to olefins, to afford biaryls, phenols, and aromatic acids, respectively. We reported previously the Pd-mediated one-step carboxylation of naphthalene with CO to give naphthoic acids in which α-naphthoic acid is formed as a main product with its β-isomer as a byproduct.[6,7] However, β-naphthoic acid is an important raw material since it easily undergoes disproportionation to give naphthalene-2,6-dicarboxylic acid which is an important starting material for synthesis of high grade polyester resins.[8] Therefore, we have investigated the reaction conditions where β-isomer is formed predominantly from CO and naphthalene via the direct C-H bond activation by Pd and found that addition of 1,10-phenanthroline gives excellent results for the selective β-isomer synthesis. In this paper we report the Pd-catalyzed selective one-step synthesis of β-naphthoic acid from CO and naphthalene.




First, in order to find out the additive which gives β-isomer selectively, we carried out the reactions using naphthalene (78 mmol), CO (1 atm), acetic acid (2.5 g), cyclohexane (1.5 g) and a variety of additives (1.0 mmol) with $Pd(OAc)_2$ (0.2 mmol) as a catalyst at 115 °C with stirring for 24-72 h. After esterification with $CH_2N_2$, the products were analyzed by GLC (OV-101,50 m,200 °C)to determine the yield and the isomer ratio. The results are listed in Table 1, and show that addition of 1,10-phenanthroline (phen) greatly increases both the yield and selectivity (the α/β-isomer ratio) of β-naphthoic acid (entry 6 vs. 7), and that even with phen,

Table 1. Effect of additives on the selective synthesis of β-naphthoic acid from CO and naphthalene[a)]

| Entry | Additive (mmol) | Reaction time/h | Yield of naphthoic acid/%[b)] | α- : β-Isomer[c)] |
|---|---|---|---|---|
| 1 | $PPh_3$ (1.0) | 24 | 30 | 60 : 40 |
| 2 | Aniline (1.0) | 24 | 0[d)] | - |
| 3 | Bipyridyl (1.0) | 24 | 16 | 51 : 49 |
| 4 | Quinoline (1.0) | 24 | 10 | 48 : 52 |
| 5 | 1,10-Phenanthroline (1.0)[e)] | 24 | 48 | 19 : 81 |
| 6 | " | 72 | 306 | 9 : 91 |
| 7 | None | 72 | 27 | 56 : 44 |
| 8 | 1,10-Phenanthroline (1.0)[e,f)] | 24 | 1.2 | 87 : 13 |

a) $Pd(OAc)_2$, 0.2 mmol; CO, 1 atm; naphthalene, 78 mmol; cyclohexane, 1.5 g; acetic acid, 2.5 g; 115 °C.
b) GC yield based on Pd.
c) The ratio of isomers was determined by GLC using a capillary column (OV-110,50m).
d) No naphthoamide was formed.
e) Monohydrate was used.
f) Naphthalene (39 mmol) and $CHCl_3$ (6 $cm^3$)were used.

Table 2. β-Naphthoic acid synthesis from CO and naphthalene by various catalysts[a)]

| Entry | Catalyst | CO ($kg/cm^2$abs) | $O_2$ ($kg/cm^2$abs) | Time/h | Yield of naphthoic acid/%[b)] | α/β-Isomer ratio[c)] |
|---|---|---|---|---|---|---|
| 1 | $Pd(OAc)_2$ | 1.0 | - | 24 | 48 | 19/81 |
| 2 | $Pd(OAc)_2$ | 0.66 | 0.34 | 20 | 421 | 8/92 |
| 3 | Pd black | 1.0 | - | 24 | 32 | 16/84 |
| 4 | Pd black | 1.0 | - | 70 | 250 | 16/84 |
| 5 | Pd black | 0.66 | 0.34 | 24 | 143 | 10/90 |
| 6 | 5% Pd-C | 1.0 | - | 24 | 9 | 8/92 |
| 7 | $Pd(acac)_2$ | 1.0 | - | 24 | 14 | 11/89 |

a) Catalyst, 0.2 mmol; phen, 1.0 mmol; naphthalene, 78 mmol; acetic acid, 2.5 g; cyclohexane, 1.5 g; 115 °C.
b) GC yield based on Pd.
c) The ratio of isomers was determined as described in Table 1.

addition of $CHCl_3$ as solvent and reduction of the charging amount of naphthalene from 79 to 39 mmol decrease the yield and the selectivity of β-isomer (entry 8).[9)]

Then we examined the catalytic activity of various Pd catalysts using phen as an additive. Table 2 summarizes the results. From the table it can be seen that not only $Pd(OAc)_2$ but also Pd-C and Pd black, the zerovalent species, are effective for carring out the direct conversion of naphthalene to β-naphthoic acid. Thus, Pd black catalyzes the reaction to afford the acids in 250% yield based on Pd and in 84% β-isomer selectivity (entry 4). This finding is interesting in a sense that these zerovalent Pd species have been considered not to be reactive to direct activation of a C-H aromatic bond under usual reaction conditions.[1,2,4,5)]

For the formation of naphthoic acid from naphthalene and CO, one more oxygen atom is needed stoichiometrically. Thus the origin of the oxygen atom in the formed naphthoic acid was investigated. The data in Table 3 show that presence of

Table 3. Effect of acetic acid and $O_2$ on the formation of naphthoic acids[a)]

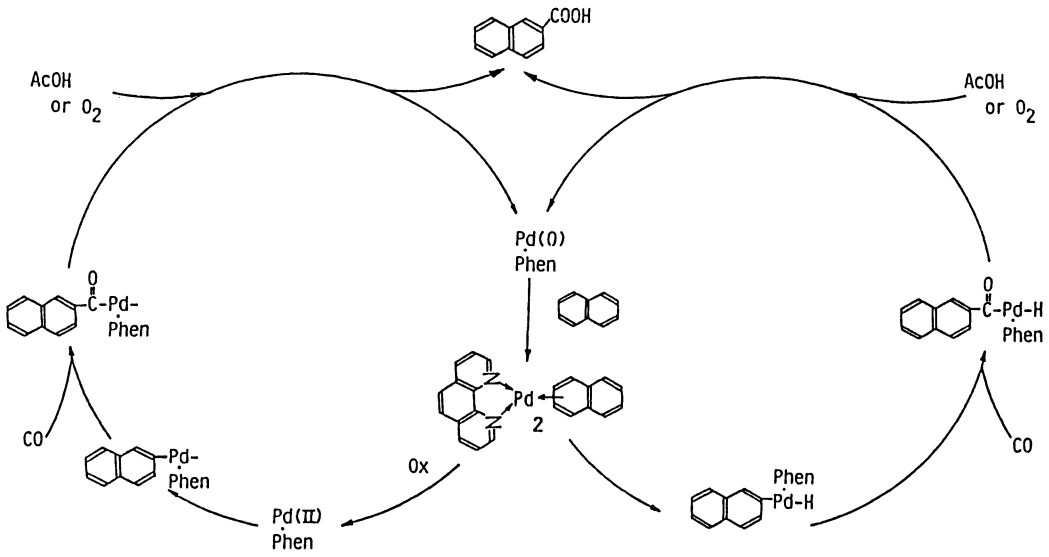
| Entry | Acetic acid (g) | CO ($kg/cm^2$abs) | $O_2$ ($kg/cm^2$abs) | Reaction time/h | Yield of naphthoic acid/%[b)] |
|---|---|---|---|---|---|
| 1 | 0 | 1.0 | 0 | 48 | 0.1 |
| 2 | 0 | 0.66 | 0.34 | 48 | 17.5 |
| 3 | 2.5 | 1.0 | - | 24 | 32 |
| 4 | 2.5 | 0.66 | 0.34 | 24 | 143 |

a) Pd black, 0.2 mmol; phen, 1.0 mmol; naphthalene, 78 mmol; cyclohexane, 1.5 g; 115 °C.

b) GC yield based on Pd.

acetic acid (entry 3) or molecular $O_2$ (entry 2) gives the acid and presence of both gives higher yield than the former cases (entry 4) whereas absence of both acetic acid and $O_2$ gives only a small amount of the acid (entry 1), suggesting that one oxygen atom in the product is derived from both acetic acid and $O_2$ molecule. The acceleration of the reaction by $O_2$ (entry 3 vs. 4) suggests that it may have another role to reoxidize Pd(0) to Pd(II) because $Pd(OAc)_2$, the divalent species is more active than Pd black or Pd-C under the similar conditions (Table 2, entry 1 vs. 3 and 6).

The formation of naphthoic acids would be explained by the reaction paths (A and B) shown in Scheme 1. Path A involves the usual electrophilic substitution of Pd(II) with naphthalene and path B involves addition of a naphthalenic C-H bond to Pd(0) which is activated by coordination of phen. That both phen and a high concentration of naphthalene are needed for selective β-isomer formation, and that absence of CO results in the formation of binaphthyls seem to indicate that these two cycles proceed via a very bulky intermediate such as **2** in which the naphthalene ligand would be attacked subsequently by Pd(II) (path A) or by Pd(0) (path B) at the sterically less-hindered β-position.




Path A: Electrophilic Substitution Path B: Oxidative Addition

Scheme 1.

One of the most characteristic features of this reaction is that the Pd/phen system catalyzes the direct carboxylation reaction of naphthalene with CO as well as the $Pd(OAc)_2$/phen system, to give β-naphthoic acid in more than 80% selectivity.

Studies on the mechanism as well as the improvement of catalytic activity and the selectivity are now under investigation.

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9) Similar dilution effect was observed when acetic acid was used in lieu of $CHCl_3$.

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