CHEMISTRY LETTERS, pp. 1865-1868, 1987.

Palladium Catalyzed Hydroxylation of Benzene with O_2 or H_2O via the C-H Aromatic Bond Activation. Preparation of Phenol

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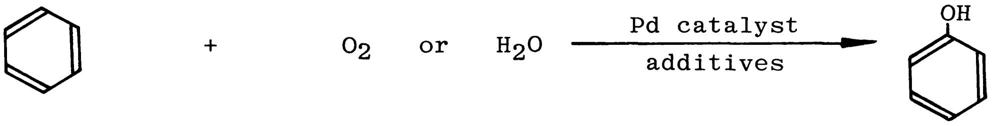
Benzene reacts with O_2 (15 bar) to give phenol directly in a high yield via the direct phenyl C-H bond activation promoted by some Pd based catalysts/CO(15 bar)/1,10-phenanthroline systems. Addition of both CO (15 bar) and phenanthroline or bipyridine is needed for the selective synthesis of phenol. Benzene also reacts with H_2O to give phenol by the catalysis of a 5% Pd-C catalyst.

We wish to describe the palladium catalyzed direct hydroxylation of benzene with O_2 or H_2O to give phenol via activation of C-H aromatic bonds.[1)] Commercially phenol has been produced mainly by the Cumene process but this process has disadvantages that it is an indirect method using benzene and propyrene as starting materials and that it gives acetone as a byproduct.[2)] Although much effort has been devoted to develop new processes which produce phenol directly from benzene and O_2,[3)] they are not satisfactory because of their severe reaction conditions or low turnover frequency of the catalysts.

We have discovered the Pd-catalyzed substitution of olefins by aromatic compounds to give aromatic-substituted olefins in one-step which proceeds via an ArPdL σ complex intermediate(**1**) derived from direct activation of a C-H aromatic bond by Pd(II).[4)] **1** has been proved to be an important synthetic intermediate, reacting with CO[5)] and CO_2,[6)] to give aromatic acids. In the course of a program aimed at the development of new reactions via the direct C-H bond activation by transition metal complexes, we have found that phenol can be prepared directly from benzene and O_2 or H_2O.



A typical reaction was carried out as follows: in a 200-cm^3 autoclave was placed a 50-cm^3 centrifuge tube containing benzene (16 cm^3), acetic acid (4 cm^3), 1,10-phenanthroline (1 mmol), and $Pd(OAc)_2$ (1 mmol) as a catalyst. The autoclave was closed and pressurized to 30 bar by CO and O_2 (15 bar each), and then the mixture was heated for 12 h at 180 °C with stirring. The results of the direct hydroxylation of benzene with O_2 by a $Pd(OAc)_2$ catalyst are shown in Table 1.

Table 1. Direct Hydroxylation of Benzene with O_2 by $Pd(OAc)_2$[a)]

Run	Benzene (cm^3)	AcOH (cm^3)	Phen[b)] (mmol)	CO (bar)	O_2 (bar)	Temp °C	Time h	Product and Yield/%[c)] PhOH	PhOAc	PhCOOH	Ph-Ph
1	16	4	1.0	15	15	180	12	502	18	0.2	0
2	16	4	1.0	15	15	150	12	27	0.2	0	0
3	20	-	1.0	15	15	180	12	3.6	0	0	0
4	16	4	1.0	-	15	180	6	0	0	0	62
5	16	4	-	15	15	180	12	40	33	169	0
6	16	4	1.0	15	-	180	12	0	0.6	4.1	0

a) $Pd(OAc)_2$, 1 mmol.

b) Phen=1,10-phenanthroline monohydrate.

c) GC yields based on Pd.

Table 2. Effect of Added Ligands on the Hydroxylation of Benzene with O_2[a)]

Run	Ligand	Product and Yield/%[b)] PhOH	PhOAc	PhCOOH	Ph-Ph
1	1,10-Phenanthroline	502	18	0.2	0
2	2,2'-Bipyridine	218	1	0	0
3	Tetraphenylporphine	0	0	0	0
4	Pyridine	0	0	0	0
5	Triphenylphosphine	0.2	1	0.8	0
6	1,2-Bis(diphenylphosphino)ethane	0.2	1.2	0.3	0
7	none	40	33	169	0

a) The reactions were carried out charging $Pd(OAc)_2$ (1 mmol), benzene (16 cm^3), AcOH (4 cm^3), the additive (1 mmol), O_2 (15 bar), and CO (15 bar) in an autoclave with stirring at 180 °C for 12 h.

b) GC yields based on Pd.

As shown in Table 1, reaction of benzene with O_2 gives phenol in 502% yield based on Pd together with phenyl acetate (18%) and benzoic acid (0.2%) as byproducts (run 1). When the temperature was allowed to decrease to 150 °C, the yield of phenol decreased to 27% (run 2), and the absence of acetic acid also decreased the yield (run 3). Interestingly enough, the lack of CO results in the sole formation of biphenyl (run 4), and the lack of 1,10-phenanthroline results in the formation of benzoic acid as a main product (run 5). These results clearly show that the addition of both CO and phenanthroline to the reaction system is essential to bring about the selective synthesis of phenol. The absence of O_2 also gives no phenol but instead, benzoic acid is formed[5)] (run 6).

It was also found that Pd black and Pd-C are also active catalysts as well as

$Pd(acac)_2$, but that $PdCl_2$ is not.

There is one possibility that phenol is formed indirectly from phenyl acetate which is produced as a byproduct since it has been known that in the presence of Pd catalysts, phenyl acetate can be oxidized to phenol under an oxygen atmosphere.7) To check this point, we carried out the reaction using phenyl acetate as a starting material. When phenyl acetate was allowed to react in acetic acid solution without benzene under the similar reaction conditions, more than 85% of the starting phenyl acetate was recovered unreacted with 13% of phenol, and when the reaction with 6.5 mmol of phenyl acetate was carried out in benzene solution, 7.5 mmol of phenol was obtained with recovery of 5.2 mmol of phenyl acetate by GC analysis. These results clearly indicate that phenol is produced via a direct hydroxylation path.

Table 2 summarizes the effect of the added ligands on the product distribution. One can see from the table that nitrogen containing bidentate ligands such as 1,10-phenanthroline and 2,2'-bipyridine are effective for selective synthesis of phenol (runs 1 and 2), and that a very rigid ligand, tetraphenylporphine with which several Mn complexes are prepared as models of cytochrome P-450 enzyme and their oxidizing ability toward benzene8a) and olefins8b) is found, inhibits the reaction (run 3).

Table 3. Hydroxylation of Benzene with H_2O

Run	Catalyst b)	H_2O (mmol)	CO (bar)	Temp °C	Time h	Product and Yield/% c) PhOH	Ph-Ph
1	5% Pd-C A	-	15	100	5	3.3	0
2	5% Pd-C B	-	15	100	5	0	0
3	5% Pd-C B	0.55	15	100	5	0.3	0
4	5% Pd-C B	5.50	15	100	5	0.6	0
5	5% Pd-C B	5.50	15	180	12	10.0	0.3
6	5% Pd-C B	5.50	- d)	180	12	0.1	2.9
7	5% Pd-C B	5.50	- e)	180	12	0.1	7.2
8	Pd black	5.50	15	180	12	0	0

a) Unless otherwise stated, the reactions were carried out charging Pd catalyst (0.5 mmol), benzene (20 cm^3), CO (15 bar), and H_2O (the amount given in this table), in an autoclave with stirring at the temperature for the period given in this table.
b) A: without drying, B: dried at 180 °C in vacuo for 5 h.
c) GC yields based on Pd.
d) Instead of CO, N_2 (15 bar) was used.
e) Instead of CO, O_2 (15 bar) was used.

We have also found that in the presence of 5% Pd-C, benzene reacts with H_2O to give phenol in low yield. The results are shown in Table 3. The formation of phenol is significantly affected by both the drying condition of the Pd-C catalyst (runs 1 and 2) and amounts of added H_2O (runs 2-5). Thus, the reaction with dried

Pd-C and without H_2O, gives no phenol (run 2). The reaction would proceed via activation of H_2O by adsorption on the surface of the catalyst. This catalyst system also requires the presence of CO for selective phenol formation, and if no CO is added, biphenyl is formed as a chief product (runs 6 and 7). The reaction with Pd black did not take place under the same conditions (run 8).

Although the mechanism of the reaction, especially the role of CO and phenanthroline, is not yet clear, CO would coordinate to **1** (Ar=Ph) and inhibits coupling of **1** with benzene to biphenyl. Another role of CO would be that it acts as an acceptor of one oxygen atom of O_2, and another oxygen atom being incorporated into phenol, thus assisting the O-O bond cleavage. In fact, an appreciable amount of CO_2 gas (31%) was detected after the reaction.

Catalyst efficiency is one of the most important aspects of this reaction. The yield of phenol increased up to 1100% based on Pd when O_2 and CO gases were repeatedly supplied to 30 bar, the initial pressure, every 8 h to replace what was consumed during the 24 h period.[9)]

Extension of the present work to other aromatic systems and studies of mechanism are in progress. Preliminary results for monosubstituted benzenes and naphthalenes show that the present reaction is also applicable to these aromatic compounds.

References

1) T. Jintoku, K. Itoh, H. Taniguchi, and Y. Fujiwara, presented in part at the 5th International Symposium on Homogeneous Catalysis, Kobe, Japan, September 22-26, 1986, Abstr., p.106.
2) The recent changes in the raw materials, for example, in MMA (methyl methacrylate) process decrease the demand of acetone: T. Hasuike and H. Matsuzawa, Hydrocarbon Process, 1979, 105.
3) S. Ito and K. Sasaki, Yuki Gosei Kagaku Kyokai Shi, 41, 839 (1983); D. A. Whiting, "Comprehensive Organic Chemistry," ed by J. F. Stoddart, Pergamon Press, Oxford (1979), p.707.
4) I. Moritani and Y. Fujiwara, Tetrahedron Lett., 1967, 1119; J. Am. Chem. Soc., 91, 7166 (1969); Nippon Kagaku Kaishi, 1985, 512.
5) Y. Fujiwara, T. Kawauchi, and H. Taniguchi, J. Chem. Soc., Chem. Commun., 1980, 220; ibid., 1982, 132; J. Organomet. Chem., 256, C35 (1983); T. Jintoku, H. Taniguchi, and Y. Fujiwara, Chem. Lett., 1987, 1159.
6) H. Sugimoto, I. Kawata, H. Taniguchi, and Y. Fujiwara, J. Organomet. Chem., 266, C44 (1984).
7) Hoechst GMBH, Bri. Pat. 1200708.
8) a) I. Tabushi and K. Morimitsu, Tetrahedron Lett., 27, 51 (1986); b) I. Tabushi and M. Kodera, J. Am. Chem. Soc., 108, 1101 (1986).
9) Carried out under the following reaction conditions: benzene; 16 cm^3, AcOH; 4 cm^3, 1,10-phenanthroline; 1 mmol, $Pd(OAc)_2$; 1 mmol, CO; 15 bar, O_2; 15 bar (initial pressure), 180 °C, 24 h.

(Received July 10, 1987)