A Selective Synthesis of Biphenyl by the $Pd(OAc)_2/MoO_2(acac)_2/O_2$/AcOH Catalyst System

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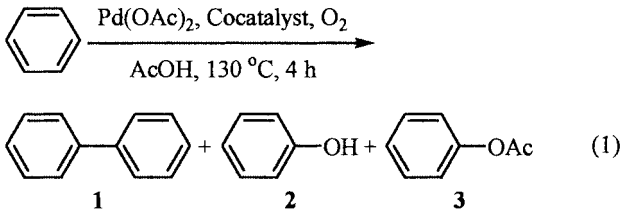
A high selectivity of biphenyl (88%) was attained by the Pd-catalyzed dimerization of benzene in the presence of O_2 and acetic acid when $MoO_2(acac)_2$ was used as a cocatalyst. Various Mo compounds gave high selectivities of biphenyl (82–87%).

Biphenyl is an important industrial material used as a heat transfer agent, an antimildew agent, or a raw material of synthetic resins.[1,2] It is presently manufactured in a vapor phase dehydrogenation of benzene.[2] However a low temperature liquid phase synthesis of biphenyl such as a catalytic dimerization of benzene is also interesting both scientifically and industrially. The Pd-catalyzed dimerization of benzene in a liquid phase has been studied extensively.[3] However there are no reports on the selectivity of biphenyl synthesis in the presence of O_2. Only the result concerning the addition of nitrogen containing bidentate ligands such as phenanthroline or bipyridine and CO to achieve a high selectivity of phenol in the Pd catalyzed direct synthesis from benzene with O_2 has been reported in this area.[4]

We have found that biphenyl can be synthesized with high selectivity (88%) by the Pd-catalyzed dimerization of benzene in the presence of $MoO_2(acac)_2$ as a cocatalyst and O_2 in acetic acid. Herein we report these results.

First, we investigated the effect of cocatalysts in the $Pd(OAc)_2$-catalyzed dimerization of benzene in the presence of O_2 and acetic acid (eq 1).



(1)

The reactions were carried out as follows: in a 100-cm^3 stainless steel autoclave equipped with a magnetic stirring bar, a pressure gauge and a thermocouple, were charged benzene and acetic acid (3 g each), 0.13 mmol of $Pd(OAc)_2$ and 0.07 mmol of a cocatalyst, and then oxygen was introduced to the appropriate pressure. The mixture was heated at 130 °C with stirring for 4 h. After the reaction the products were analyzed by gas chromatography. The results are summarized in Table 1.

From the data of this table, one can see that $MoO_2(acac)_2$ is the best cocatalyst for Pd compared with other metals examined giving 86% biphenyl selectivity (entry 8). $Zr(acac)_4$ and $Pr(OAc)_3{\cdot}2H_2O$ (entries 7 and 6) are next best but $LiOAc{\cdot}2H_2O$, $Mg(OAc)_2{\cdot}4H_2O$, $Al(acac)_3$ and $Be(acac)_2$ showed inferior results.

Table 1. Effect of cocatalysts[a]

Entry	Cocatalyst	Product /mmol[b]			1/(1+2+3) /%
		1	2	3	
1	None	0.47	0.44	0.03	50
2	$LiOAc{\cdot}2H_2O$	0.62	0.36	0.03	62
3	$Be(acac)_2$	0.63	0.61	0.06	49
4	$Mg(OAc)_2{\cdot}4H_2O$	0.61	0.33	0.04	62
5	$Al(acac)_3$	0.56	0.54	0.07	48
6	$Pr(OAc)_3{\cdot}2H_2O$	0.56	0.17	0.02	75
7	$Zr(acac)_4$	0.81	0.21	0.04	77
8	$MoO_2(acac)_2$	0.77	0.08	0.05	86
9[c]	$MoO_2(acac)_2$	1.29	0.08	0.08	88

[a]Reaction conditions: Stainless steel autoclave (100 mL), $Pd(OAc)_2$ (0.13 mmol), cocatalyst (0.07 mmol), AcOH (3.0 g), benzene (38 mmol), O_2 (10 atm), 130 °C, 4 h. [b]Determined by GC. [c]$Pd(OAc)_2$ (0.31 mmol).

It is known that dimerization of benzene proceeds via a Pd–phenyl σ-complex intermediate.[5] Thus, the higher concentration of Pd would favor the formation of σ-complex which reacts with benzene molecule to give the higher biphenyl selectivity.

We examined the effect of the amount of $Pd(OAc)_2$ on the reaction (entries 8 and 9). This idea was supported by the result to give the highest selectivity (88%) when the amount of $Pd(OAc)_2$ was the highest with $MoO_2(acac)_2$ (entry 9).

Since it became apparent that $MoO_2(acac)_2$ has high activity as a cocatalyst, we further studied the activity of molybdenum compounds together with titanium compounds.

Table 2. Effect of various Mo and Ti compounds[a]

Entry	Cocatalyst	Product /mmol[b]			1/(1+2+3) /%
		1	2	3	
1	$TiO(acac)_2$	0.76	0.11	0.13	76
2	TiO_2	0.43	0.12	0.02	76
3	MoO_3	0.44	0.04	0.02	87
4	$MoCl_5$	0.22	0.05	0.00	83
5	MoO_2	0.51	0.08	0.03	82

[a] Reaction conditions: Stainless steel autoclave (100 mL), $Pd(OAc)_2$ (0.13 mmol), cocatalyst (0.07 mmol), AcOH (3.0 g), benzene (38 mmol), O_2 (10 atm), 130 °C, 4 h. [b] Determined by GC.

Table 2 summarizes the results. Molybdenum compounds such as Mo(IV)O_2, Mo(V)Cl_5, and Mo(VI)O_3 give high selectivities of biphenyl (82–87%) (entries 5, 4 and 3) and titanium (IV) compounds such as TiO_2 and TiO(acac)$_2$ are also found to give a high selectivity (76%).

These results suggest that the high selectivity of biphenyl is attained by increasing the formation of biphenyl and suppressing that of phenol in Mo and Ti acetylacetonate compounds. In the absence of an acetylacetonate (acac) ligand, cocatalysts such as TiO_2 and MoO_3, do not actually increase the formation of biphenyl, but suppress that of phenol.

In order to obtain the information on the role of Mo and an active intermediate between Pd and Mo, we made a study of the amount of MoO_2(acac)$_2$.

Figure 1 shows the effect of the amount of MoO_2(acac)$_2$ on the biphenyl and phenol formation.

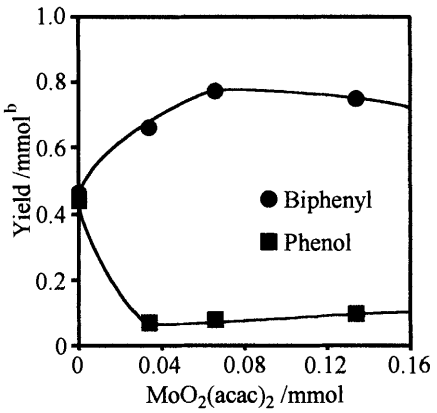


Figure 1. Effect of the amount of MoO_2(acac)$_2$.[a]

[a]Reaction conditions: Stainless steel autoclave (100 mL), Pd(OAc)$_2$ (0.13 mmol), AcOH (3.0 g), benzene (38 mmol), O_2 (10 atm), 130 °C, 4 h. [b]Determined by GC.

The yield of biphenyl increases with the increasing amount of MoO_2(acac)$_2$ until it reaches 0.07 mmol, and then becomes constant. This result suggests the formation of some kind of Pd–Mo complex.

When an equal molar amount of acetylacetone was used instead of a cocatalyst, the reaction itself was accelerated about 40% more. However, the selectivity of biphenyl decreased to 47%.

In conclusion, it was found that MoO_2(acac)$_2$ gave the best selectivity of biphenyl suggesting the formation of a highly positive center with Pd in the ratio of 1 to 2 to increase the formation of biphenyl and suppress that of phenol. The mechanistic investigation from the metal complex formation and kinetics is underway.

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