Palladium-Mediated Carbonylation and Coupling Reactions of Iodobenzene and Aniline. Model Reactions for the Preparation of Aromatic Polyamides

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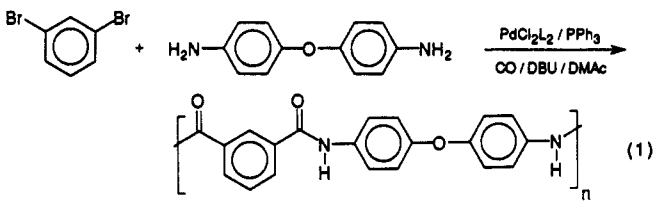
ABSTRACT: The carbonylation and coupling reaction of iodobenzene and aniline to form *N*-phenylbenzamide was examined as a model system for the preparation of aromatic polyamides (aramids). Variables such as carbon monoxide (CO) pressure, temperature, catalyst type and loading, ligand level, solvent, substituents, and neutralizing base were evaluated in the optimization process. It was found that clean, quantitative formation of *N*-phenylbenzamide occurred in 0.5 h in a DMAc solution using 3% $PdCl_2L_2$ (L = PPh_3), 90 psig CO, 115 °C, and 1.2 equiv of DBU. Dimers from *m*-diiodobenzene and *p*-toluidine or *m*-phenylenediamine and *p*-iodotoluene also formed cleanly and were isolated in yields of greater than 95%.

Introduction

Interest in aromatic polyamides (aramids) has been maintained in the high-performance fibers industry because of their low weight, high modulus, thermal stability, and solvent resistance. Aramids have been conventionally prepared through the reaction of diacid chlorides and diamines at low temperatures.[1] Recently, a report appeared on the synthesis of modest molecular weight aramids by the palladium-catalyzed carbonylation and coupling reaction of diamines and aromatic dibromides (eq 1).[2]



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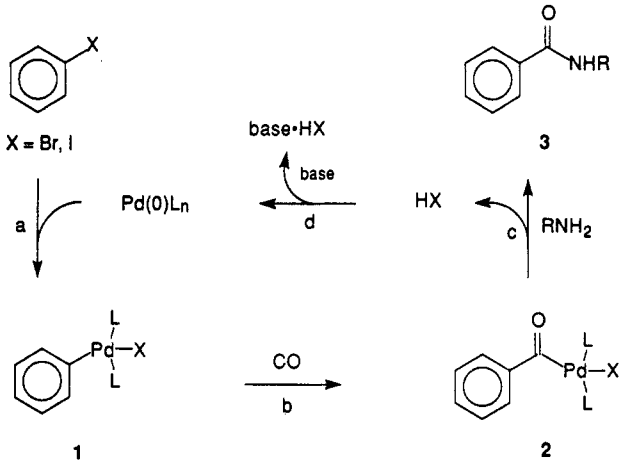
Aromatic iodides are known to be excellent substrates for preparing amides via the carbonylative coupling reaction.[3] Recent reports have disclosed the facile regioselective preparation of diiodoaromatic compounds.[4] The availability of these key intermediates prompted us to undertake a study of the reactivity of iodoaromatics and amines with the goal of producing high molecular weight aromatic polyamides. This paper reports the details of the model amidation reaction of iodobenzene and aniline. The polymerization study follows in the subsequent paper.

Results and Discussion

To understand the nature of the carbonylation reaction and its application toward aramid formation, an extensive study of *N*-phenylbenzamide formation from aniline and iodobenzene was undertaken. In 1974, Heck reported that treatment of aromatic halides (bromides and iodides) with a catalytic amount of a palladium(0) or palladium(II) species and a primary or secondary amine in the presence of carbon monoxide (CO) and a base produced amides in good yield.[3] The mechanism of amide formation as outlined in Scheme I involves a coordinatively unsaturated Pd(0) species oxidatively adding to the aromatic halide, producing a Pd(II) complex 1. Carbon monoxide then

Scheme I



inserts in the aryl–palladium bond giving acyl complex 2. This is followed by attack of the amine leading to the regeneration of the active Pd(0) catalyst and liberation of the free amide 3.[3,5] (An alternate possibility involves nucleophilic attack of the amine on a coordinated CO bound to the arylpalladium complex 1 to give an (arylcarbamoyl)palladium intermediate. This route has been established as a pathway when secondary aliphatic amines are used.)[6] In this scheme L represents unspecified ligands, usually phosphines, amines, or CO.

The literature reveals that aryl bromides are the substrates generally chosen for amide formation and that reactions are commonly run at 100 °C under 1 atm of CO and in the presence of a tertiary amine, usually tributylamine. Reaction times are in the range from 2 to 10 h and give good yields of products.[3] A number of variables can influence the yield and rate of amide formation. These include solvent, temperature, CO pressure, type of catalyst and associated ligands, catalyst loading, and neutralizing base. We wished to see how these variables affected amide formation from aryl iodides. In all cases, the reaction under consideration is the carbonylation of iodobenzene and condensation with aniline to form *N*-phenylbenzamide (eq 2). Reactions were run on approximately a 2-mmol scale with aliquots removed at timed intervals for GC analysis.

Effect of CO Pressure

It is well documented that zero-valent palladium compounds undergo oxidative addition to aryl iodides faster

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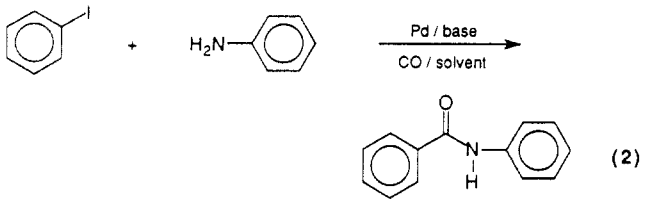


(2)

than the corresponding aryl bromides.[7] In ester formation with aryl bromides[8] oxidative addition is the rate-limiting step[9] (step a in Scheme I) and for this reason only 1 atm of CO is employed. At higher CO pressures, the Pd(0) species will be coordinated by a greater number of CO molecules[10] rendering the palladium less nucleophilic and therefore less prone to undergo oxidative addition.[11] With aryl iodides, the rate-limiting step, at least in α-keto amide formation, is CO insertion.[12] This suggests that the rate could be increased under higher CO pressures.

Figure 1 illustrates that, under 1 atm of CO at 115 °C and 6% catalyst ($PdCl_2L_2$) loading, formation of *N*-phenylbenzamide is complete after 0.75 h. When the CO pressure was increased to 40 psig, the reaction time was cut to 0.5 h, and at 90 psig (the practical limits to the reaction vessel) the time had dropped to 0.2 h. Thus, a 3-fold increase in rate was achieved by increasing the CO pressure from 1 to about 6 atm. In contrast, reactions with bromobenzene and aniline behaved in the opposite manner. Under 1 atm of CO pressure, complete amidation occurred within 0.5 h. At 40 psig CO, it took 3 h and, at 90 psig, 4.5 h for complete reaction. These observations add to the body of evidence cited above that suggests CO insertion is, or contributes to, the rate-limiting step (rls) in amidation reactions with iodoaromatics, whereas oxidative addition is the determining factor in reactions with bromoaromatics.

Given the slightly faster reaction times of iodobenzene at high CO pressures versus bromobenzene at low pressures and the ready availability of bisiodinated aromatics,[4] the remainder of the amidation reactions were carried out with iodobenzene at elevated CO pressures. It is expected that higher CO pressures will continue to result in a rate increase until the point is reached where the concentration of reactive Pd(0) species is diminished so as to make oxidative addition a slower step than the subsequent CO insertion as described for the aryl bromides. This rate enhancement has been seen in a kinetic study of the carboxymethylation of aryl iodides.[13] In that report, maximum rates were seen to occur between 6 and 60 atm of CO depending on the nature of other aryl substituents.

Temperature

As expected, an increase in reaction temperatures resulted in faster product formation. Figure 2 shows that *N*-phenylbenzamide formation was complete in less than 1 h at 65 °C. At 90 °C, 25 min was enough and only 15 min was required at 115 °C. When the temperature was raised to 150 °C, the reaction was complete within 3 min. Temperatures exceeding 150 °C were not examined because of the rapidity of the reaction at this temperature. However, the reagents are stable to 190 °C, and temperatures this high could be used if necessary. Facile amide formation at lower temperatures may be an asset if competing side reactions are present in this or the polymer system.

Catalyst Loading

Three levels of catalyst were examined at two temperatures to document the effect of catalyst concentration on

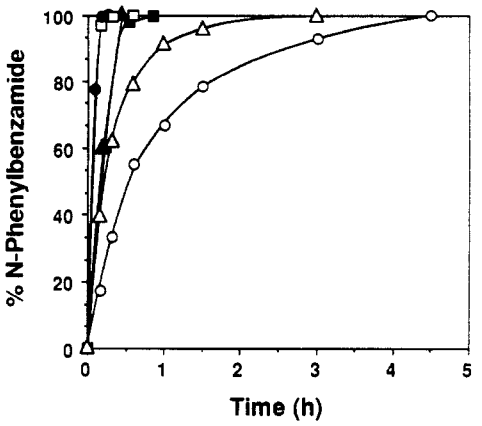


Figure 1. Effect of CO pressure on *N*-phenylbenzamide formation from iodo- or bromobenzene. Reaction in DMAc (0.33 M), 115 °C, 6% $PdCl_2L_2$, 12% PPh_3, and 1.2 equiv of DBU. (■) 1 atm, iodo; (▲) 40 psig, iodo; (●) 90 psig, iodo; (□) 1 atm, bromo; (△) 40 psig, bromo; (○) 90 psig, bromo.

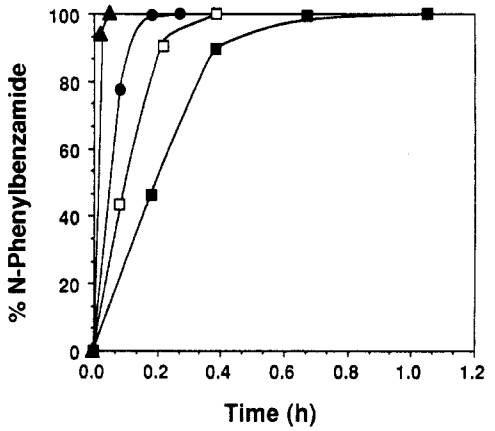


Figure 2. Effect of temperature on *N*-phenylbenzamide formation. Reaction in DMAc (0.33 M), 90 psig CO, 6% $PdCl_2L_2$, 12% PPh_3, and 1.2 equiv of DBU. (■) 65 °C, (□) 90 °C, (●) 115 °C, (▲) 150 °C.

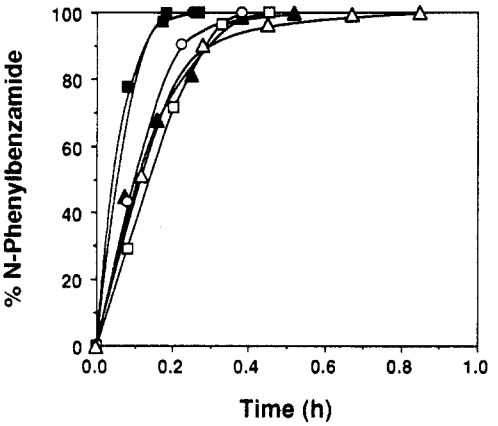


Figure 3. Effect of catalyst loading on *N*-phenylbenzamide formation. Reaction in DMAc (0.33 M), 90 psig CO, $PdCl_2L_2$ catalyst with 2 PPh_3, and 1.2 equiv of DBU. (▲) 1% at 115 °C, (●) 3% at 115 °C, (■) 6% at 115 °C, (△) 1% at 90 °C, (○) 3% at 90 °C, (□) 6% at 90 °C.

product formation (Figure 3). At 115 °C, 1% catalyst allowed the reaction to go to completion in 25–30 min. At 3% and 6% the reaction was over in 15 min. To see if a more pronounced effect could be seen at slightly lower temperatures, the same catalyst concentrations were examined at 90 °C. At this lower temperature, the 1% reaction took almost twice as long, ca. 45 min. Again there was little difference between the 3% and 6% reactions with completion times of 27 and 23 min, respectively. With

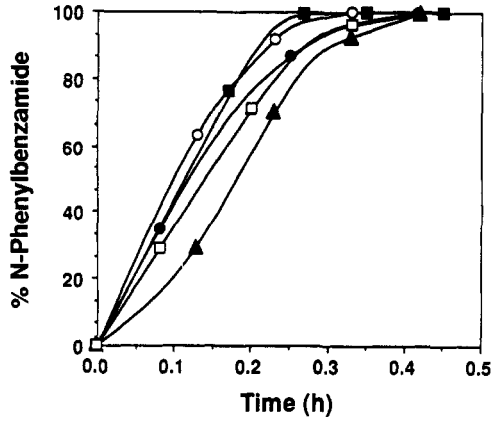


Figure 4. Effect of catalyst on *N*-phenylbenzamide formation. Reaction in DMAc (0.33 M), 90 psig CO, 90 °C, 3% catalyst, and 1.2 equiv of DBU. (▲) $Pd(OAc)_2/4L$, (□) $PdCl_2L_2/2L$, (●) $PdCl_2(PhCN)_2/4L$, (■) PdL_4, (○) $PdCl_2/4L$.

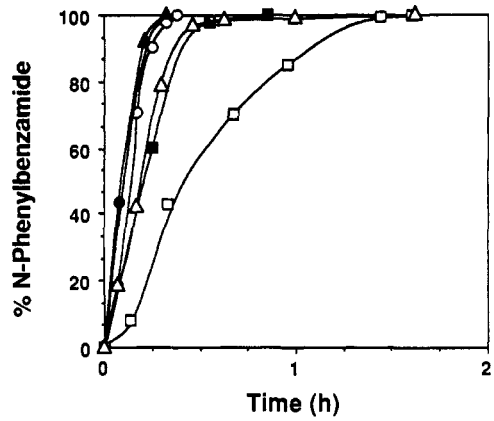


Figure 5. Phosphine ligand effect on *N*-phenylbenzamide formation. Reaction in DMAc (0.33 M) and 1.2 equiv of DBU. (■) 1 atm CO, 115 °C, 6% $PdCl_2L_2$, 12% PPh_3; (□) 1 atm CO, 115 °C, 6% $PdCl_2L_2$; (●) 90 psig CO, 90 °C, 3% $PdCl_2L_2$, 6% PPh_3; (○) 90 psig CO, 90 °C, 3% $PdCl_2L_2$; (▲) 90 psig CO, 90 °C, 3% $PdCl_2$, 12% PPh_3; (△) 90 psig CO, 90 °C, 3% $PdCl_2$.

the information compiled from the catalyst loading and temperature experiments, reaction parameters of 90 psig CO at 90 °C with 3% catalyst loading seemed appropriate for further investigation into the effects of other variables on this reaction.

Catalyst

Both Pd(0) and Pd(II) complexes may be used to catalyze the amidation reaction. The most common zero-valent palladium complex is tetrakis(triphenylphosphine)palladium(0) (PdL_4). While very reactive owing to the facile dissociation of the phosphine ligands, PdL_4 is unstable in air and slowly oxidizes.[14] Freshly prepared or newly opened ampules of this material are effective catalysts for this reaction (Figure 4), which is complete in about 15 min. However, after several days, the catalytic activity of this compound decreased even when stored under nitrogen in a refrigerator.

Palladium(II) salts are commercially available or easily prepared[14] and are less susceptible to oxidation than are Pd(0) complexes. Palladium(II) chloride ($PdCl_2$), with 4 equiv (based on palladium) of triphenylphosphine present, allowed the model reaction to go to completion in about 20 min. This complex is reported to be more toxic than other Pd(II) salts[15] and, in light of equal performance by other catalysts, was not examined further.

Reactions with palladium(II) chloride bis(benzonitrile) [$PdCl_2(PhCN)_2$] or palladium(II) chloride bis(triphenylphosphine) ($PdCl_2L_2$) and 2 equiv of triphenylphosphine present gave almost identical rates of reaction with completion times of 25 min. Both reagents are somewhat hygroscopic but can be handled in air and stored for extended periods of time under dry nitrogen. The palladium(II) acetate [$Pd(OAc)_2$] catalyzed reaction appeared to start more slowly than the others although the reaction was complete in 25 min. In all cases the number of phosphine ligands per palladium atom was kept constant at 4:1 through the addition of free triphenylphosphine.

Ligand

One of the main reasons for the introduction of phosphine ligands was to stabilize the zero-valent palladium. If not enough strongly coordinating ligands are available, then the palladium precipitates as finely divided metal. Too many ligands result in a Pd(0) complex unable to achieve the necessary reactive 14 or 16 electron coordinatively unsaturated state. The phosphines also serve as electron-donating groups, which increase the nucleophilicity of the palladium. A delicate balance must be achieved between the number of phosphine and CO ligands. As mentioned above, four phosphines were present in the reaction mixture for every palladium introduced. There are many cases in which CO or amines[5] may also serve as coordinating ligands in Group 10 transition-metal compounds.

It has been observed that phosphines are required for amide formation to take place at a reasonable rate, under 1 atm of CO. No examination of this reaction under higher CO pressure had been undertaken, and it was likely to expect that fewer phosphine ligands might be required for reaction to occur.

At 1 atm of CO, 115 °C, and 6% loading of $PdCl_2L_2$ with two additional phosphines, the model reaction was complete in less than 1 h (Figure 5). The same reaction run without the additional phosphines took 1.75 h. In contrast, under 90 psig CO, 90 °C, and 3% loading of $PdCl_2L_2$, the amide-forming reaction was complete in 25 min with or without the addition of the extra two phosphine ligands. Apparently the higher pressures of CO effectively replaced the 2 equiv of triphenylphosphine in their role as ligands. With no phosphines present, as in the $PdCl_2$-catalyzed reaction, the time for greater than 98% completion was about 35 min. When $PdCl_2$ was used with four ligands present, the total time was 22 min. While not as great an effect was noticed at 90 psig as at 1 atm., it is clear that it is advantageous to have at least two phosphines present in the reaction mixture for each palladium. Palladium metal precipitated from the $PdCl_2$-catalyzed reaction upon addition of the base. In spite of this the reaction still proceeded at a reasonably rapid pace. This leads one to believe that higher pressures might result in faster rates yet with no phosphine present.

Solvent

The first Heck amidation reactions were run neat,[3] which is practical if the aryl halide, the amine, and the base are all liquids. However, in light of the anticipated application of this chemistry toward the synthesis of aramids, in which the monomers can be high melting solids, several solvents were chosen for evaluation. Three dipolar aprotic solvents, *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), and *N*-methylpyrrolidinone (NMP), were examined for their influence on the amidation reaction, as were the two ethereal solvents tetrahydrofuran (THF) and bis(methoxyethyl) ether (diglyme). The lowest boiling solvent, THF, gave the longest reaction time, about 1.5

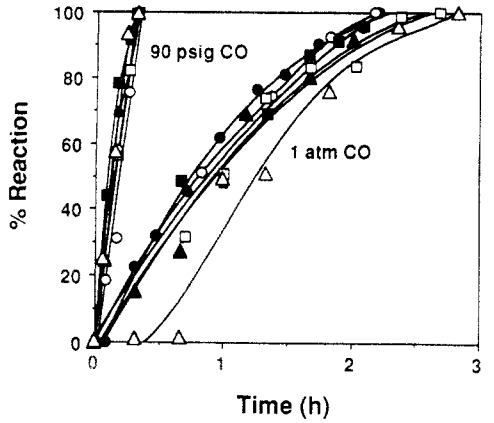


Figure 6. Aniline substituent effect on *N*-arylbenzamide formation. Reaction in DMAc (0.33 M), 1 atm or 90 psig CO, 90 °C, 3% $PdCl_2L_2$, 6% PPh_3, and 1.2 equiv of DBU. (■) OCH_3, (●) CH_3, (▲) H, (□) $COCH_3$, (○) $COOCH_3$, (△) CN.

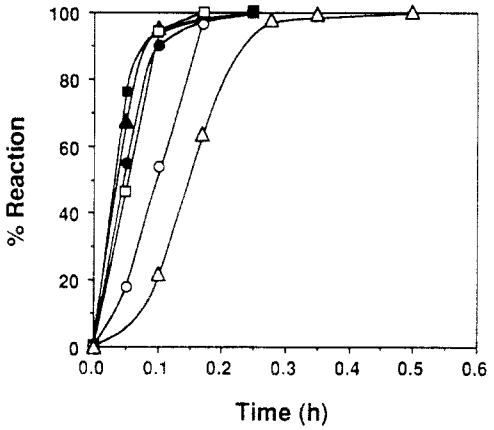


Figure 7. Iodobenzene substituent effect on *N*-phenylarylamide formation. Reaction in DMAc (0.33 M), 90 psig CO, 115 °C, 3% $PdCl_2L_2$, and 1.2 equiv of DBU. (■) OCH_3, (●) CH_3, (▲) H, (□) Cl, (●) $COOCH_3$, (△) CN.

h, while the companion ether, diglyme, was much faster, at 30 min. DMAc and DMF were also complete in 30 min as opposed to 50 min for NMP. All reactions permitted clean formation of *N*-phenylbenzamide.

Substituents

A variety of substituted anilines were examined as numerous aromatic diamines are available commercially that possess a wide range of reactivities. At 1 atm. of CO, there was a slight difference in the time for complete formation of *N*-phenylbenzamide between the strongly electron-rich *p*-anisole and electron-deficient *p*-cyanoaniline. Other substituted anilines with intermediate σ_p values, such as carbomethoxy, acetyl, and methyl derivatives, essentially reacted at the same rate. At 90 psig CO, the reactions were over quickly but little difference in reactivity was seen between the various anilines (Figure 6). This was further evidence for CO insertion being the rate-determining step under these conditions.

Little effect on the rate of amide formation was observed when reactions of electron-rich and moderately electron-poor substituted iodobenzenes and aniline were investigated (Figure 7). When strongly electron-withdrawing substituents, such as carbomethoxy or cyano, were present, a noticeable diminution in rate was seen. This may indicate that the oxidative addition of the palladium(0) catalyst to the aryl iodide or the migratory insertion reaction of the aryl group to the CO is taking part in the rate-limiting step. However, CO insertion still plays a role as witnessed

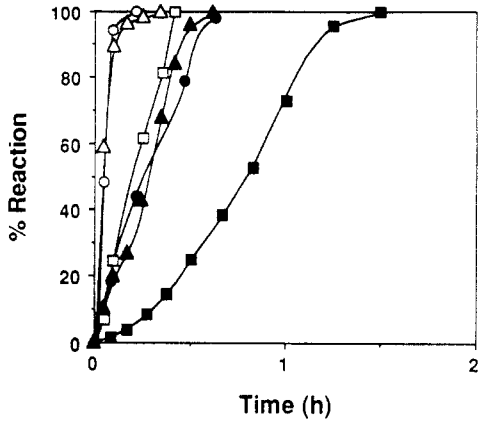


Figure 8. Substituent effect on *N*-phenylarylamide formation. Reaction in DMAc (0.33 M), 1 atm or 90 psig CO, 115 °C, 3% $PdCl_2L_2$, 6% PPh_3, and 1.2 equiv of DBU. (▲) OCH_3 (1 atm), (●) H (1 atm), (■) CN (1 atm), (△) OCH_3 (90 psig), (○) H (90 psig), (□) CN (90 psig).

Table I
Effect of Base on Amidation Reaction

entry	base	pK_a[a]	time (h)[b]
1	MTBD	13.0	0.1
2	DBU	11.9	0.2
3	DBN	11.0	0.6
4	Bu_3N	10.9	7.7[c]
5	DMAP	9.7	6.2
6	DABCO	8.2	6.5[d]
7	2,6-lutidine	6.6	7.6[e]
8	pyridine	5.2	7.2[f]

[a] Reference 16. [b] Time for complete conversion to *N*-phenylbenzamide. [c] After this time only 28% *N*-phenylbenzamide had been formed. [d] After this time only 79% *N*-phenylbenzamide had been formed. [e] After this time only 12% *N*-phenylbenzamide had been formed. [f] After this time only 8% *N*-phenylbenzamide had been formed.

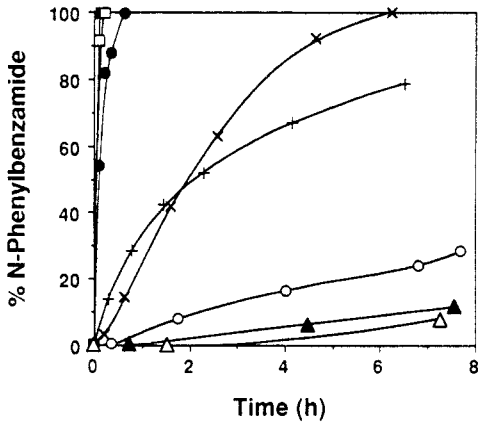


Figure 9. Effect of base on *N*-phenylbenzamide formation. Reaction in DMAc (0.33 M), 90 psig CO, 90 °C, 3% catalyst, and 1.2 equiv of base. (■) MTBD, (□) DBU, (●) DBN, (○) Bu_3N, (×) DMAP, (+) DABCO, (▲) 2,6-lutidine, (△) pyridine.

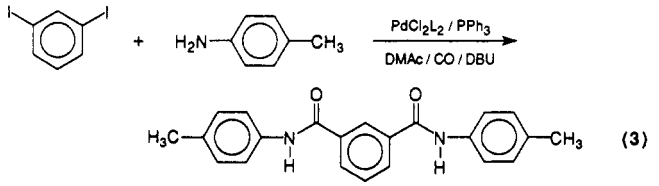
by the decrease in rate on going from 90 psig CO to 1 atm (Figure 8).

Base

The choice of base was crucial in the amidation reaction. Table I and Figure 9 show that strong bases such as MTBD, DBU, and DBN allowed clean, quantitative, rapid formation of *N*-phenylbenzamide (entries 1–3). Reactions in which bases with intermediate pK_a values, like DMAP and DABCO (entries 5 and 6), were used were much slower. Weak bases such as 2,6-lutidine and pyridine (entries 7 and 8) gave little product after 7 h of reaction. With the

exception of tributylamine (entry 4), the trend was to see an increased rate of amide formation with increasing base strength. The use of a catalytic amount (10%) of DBU and 1.2 equiv of 2,6-lutidine gave only 10% formation of product in 2 h. After 4 h, 14% *N*-phenylbenzamide had been formed.

From the aforementioned results, the optimum conditions found for *N*-phenylbenzamide formation from iodobenzene and aniline were as follows: 90–115 °C in DMAc under 90 psig CO with 1–3% palladium catalyst containing two phosphine ligands and DBU as the base. Using these conditions, dimers **4** and **5** were isolated in yields of 95 and 98%, respectively. With these guidelines we began to investigate the polymerization reactions that are reported in the following paper.



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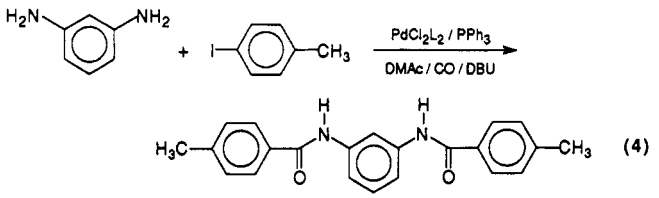

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Summary

The carbonylation and coupling reaction between iodobenzene and aniline was optimized to give quantitative formation of *N*-phenylbenzamide in 0.5 h. The effects of CO pressure, temperature, catalyst type and loading, ligands, substituents, bases, and solvent were examined. It was found that elevated CO pressures greatly increased the rate of amide formation and that strong tertiary amine bases were necessary for clean, quantitative reactions. Extension of this chemistry to the formation of bisamides was successful, giving greater than 95% isolated yields of dimers **4** and **5**.

Experimental Section

General Procedures. Reactions were performed in a 120-mL pressure reaction vessel (containing a Teflon-coated stirbar), fitted with a pressure gauge, a pressure release valve, a gas inlet, and a straight ball valve for degassing and sample withdrawal.

All reactions were monitored on an HP 5890 gas chromatograph using a 15-m, 0.25-μm DB-5 column (0.32 mm i.d.) and a flame ionization detector. Helium flow rate through the column was 4.0 mL/min. The GC parameters employed for analysis were as follows: injection port, 300 °C; detector, 350 °C; temperature ramp from 50 °C (hold 1 min) to 300 °C (hold 10 min) at 20 °C/min. Relative response factors for equimolar amounts of iodobenzene, aniline, and *N*-phenylbenzamide were within 3–4% of each other. Peak integrations were therefore taken as relative molar ratios in calculating percent completion of reaction. ^{1}H NMR and ^{13}C NMR spectra were acquired on a 300-MHz spectrometer using DMSO-d_6 as both solvent and reference. Fourier transform infrared spectra were recorded as KBr pellets.

Chemicals. Iodobenzene was fractionally distilled and stored in the presence of copper wire. Aniline, 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU), pyridine, 2,6-lutidine, and tributylamine (Bu_3N) were fractionally distilled under reduced pressure. THF was freshly distilled from Na/benzophenone ketyl, and bis-(methoxyethyl) ether (diglyme) was distilled from CaH_2. Triphenylphosphine (PPh_3) was recrystallized from hexanes, *m*-diiodobenzene was recrystallized from EtOH, and *m*-phenylenediamine was sublimed prior to use. 4-Iodotoluene, 4-iodobenzonitrile, 4-iodoanisole, 4-iodobenzoic acid, *p*-toluidine, methyl *p*-aminobenzoate, *p*-anisidine, 4′-aminoacetophenone, *p*-aminobenzonitrile (all Kodak), 1,4-diazabicyclo[2.2.2]octane (DABCO), (*N*,*N*-dimethylamino)pyridine (DMAP), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), *N*,*N*-dimethylacetamide (DMAc, anhydrous), *N*,*N*-dimethylformamide (DMF, anhydrous), *N*-methylpyrrolidinone (NMP, anhydrous), 4-iodochlorobenzene (all Aldrich), 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD, Fluka), and CO (Air Products, UPC grade) were all used as received. All palladium catalysts, [bis(triphenylphosphine)palladium(II) chloride ($PdCl_2L_2$), palladium acetate ($Pd(OAc)_2$), palladium chloride bis(benzonitrile) ($PdCl_2$·2BzCN), palladium chloride ($PdCl_2$), tetrakis(triphenylphosphine)palladium (PdL_4), were obtained from Aldrich and used as received.

Typical Reaction. To a clean, dry pressure vessel under an argon purge were added iodobenzene (200 μL, 1.79 mmol), aniline (163 μL, 1.79 mmol), PPh_3 (28 mg, 0.107 mmol, 3%), $PdCl_2L_2$ (38 mg, 0.053 mmol), and DMAc (5.4 mL, 0.33M). The bottle was sealed and flushed with CO. The contents of the bottle were then degassed and filled with argon three times. The final degassing was followed by the introduction of CO, which saturated the solution. The contents of the reactor were then stirred and heated to 90 °C in a thermostated oil bath until all the solids had dissolved. At this time any pressure in the reactor was released and DBU (320 μL, 2.14 mmol, 1.2 equiv) was added by syringe through the ball valve. The flask was again flushed with CO and pressurized to 90 psig. Samples were withdrawn at timed intervals and diluted in THF for GC analysis.

***N*,*N*′-Di-*p*-tolylisophthalamide (4).** *m*-Diiodobenzene (990 mg, 3.00 mmol), *p*-toluidine (643 mg, 6.00 mmol), $PdCl_2L_2$ (63 mg, 0.09 mmol), PPh_3 (47 mg, 0.18 mmol), DBU (1.08 mL, 7.20 mmol), and DMAc (15 mL) were added together and treated as above, allowing the reaction to proceed for 24 h at 115 °C at 95 psig CO. The reaction mixture was filtered, concentrated in vacuo, dissolved in warm THF, and then precipitated into water. After extensive washing with water, the crystals were dried in vacuo (100 °C, 1 h) to give 1.102 g of solid (106.7% of theory). The solid was contaminated with triphenylphosphine and triphenylphosphine oxide. After removal of these contaminants, the yield was 97.5%. Mp: 268–269.5 °C. ^{1}H NMR (DMSO-d_6): δ 10.33 (s, 2), 8.49 (s, 1), 8.10 (dd, J = 8.0, 1.1 Hz, 2), 7.66 (d, J = 8.3 Hz, 4), 7.64 (m, 1), 7.14 (d, J = 8.3 Hz, 4), 2.26 (s, 6). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 164.9, 136.5, 135.3, 132.8, 130.5, 129.1, 128.6, 126.9, 120.4, 20.5. Anal. Calcd for $C_{22}H_{20}N_2O_2$: C, 76.72; H, 5.85; N, 8.13. Found: C, 76.08; H, 5.78; N, 8.01.

***N*,*N*′-Bis(4-methylbenzoyl)-1,3-phenylenediamine (5).** *m*-Phenylenediamine (324 mg, 3.00 mmol), 4-iodotoluene (1.308 g, 6.00 mmol), $PdCl_2L_2$ (63 mg, 0.09 mmol), PPh_3 (47 mg, 0.18 mmol), DBU (1.08 mL, 7.20 mmol), and DMAc (15 mL) were added together and treated as above, allowing the reaction to proceed for 24 h at 115 °C at 95 psig CO. After isolation as described above, 1.131 g of solid (109.5% of theory) was obtained. The solid was contaminated with triphenylphosphine and triphenylphosphine oxide. After removal of these contaminants, the yield was 95.4%. Mp: 248–250 °C. ^{1}H NMR (DMSO-d_6): δ 10.21 (s, 2), 8.33 (s, 1), 7.88 (d, J = 8.1 Hz, 4), 7.48 (dd, J = 8.1, 1.6 Hz, 2), 7.30 (d, J = 8.1 Hz, 4), 7.27 (m, 1), 2.35 (s, 6). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 165.4, 141.6, 139.4, 132.1, 128.9, 128.5, 127.7, 116.0, 113.0, 21.0. Anal. Calcd for $C_{22}H_{20}N_2O_2$: C, 76.72; H, 5.85; N, 8.13. Found: C, 76.55; H, 5.80; N, 8.11.

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