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Synthesis of N-Substituted Isoindolin-1-ones via Palladium-Catalyzed Carbonylative Heterocyclization of *o*-Bromobenzylbromide with Carbon Monoxide and Primary Amines

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A convenient method for the synthesis of N-substituted isoindolin-1-ones is disclosed in palladium(0)-catalyzed heterocyclization of *o*-bromobenzylbromide with carbon monoxide (CO) and primary amines in DMF at 100 °C.

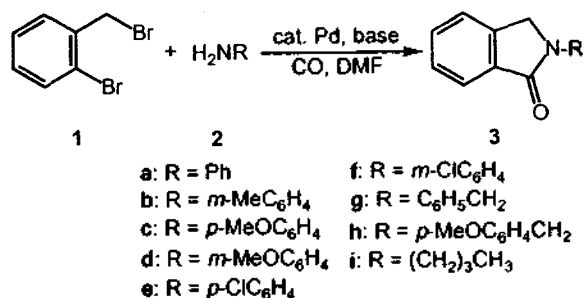
Introduction

Transition metal-catalyzed carbonylative heterocyclization has been a useful synthetic tool for the formation of a variety of heterocyclic compounds.¹ Thus, the carbonylative cyclization has been effectively applied to the synthesis of isoindolin-1-ones; *i.e.* the cobalt-catalyzed carbonylative cyclization of Schiff's bases with CO,² the carbonylation of *o*-palladated benzaldimines and tertiary benzylic amines,³ the palladium-catalyzed carbonylative cyclization of *N*-benzyl-*o*-bromobenzylamine with CO,⁴ and the cobalt-catalyzed carbonylative cyclization of *o*-bromobenzylamines with CO under sunlamp-irradiated phase transfer catalyst (PTC) conditions.⁵ On the

other hand, as part of our series of studies on the transition metal-catalyzed heterocyclization,⁶ we have now found that *o*-bromobenzylbromide reacts with CO and primary amines in DMF in the presence of a catalytic amount of a palladium compound to afford the corresponding isoindolin-1-ones in good yields. The results presented here lead to the one pot procedure for the synthesis of the N-substituted isoindolin-1-ones from three components, *o*-bromobenzylbromide, primary amines, and CO.

Results and Discussion

Although Mori⁴ and Brunet⁵ partly investigated the transi-



Scheme 1.

Table 1. Palladium-Catalyzed Reaction of *o*-Bromobenzylbromide (1) with Aniline (2a) and CO under Various Conditions^a

Run	Palladium salt	Base	Conditions		Yield (%) ^b of 3a
			°C	CO (atm)	
1	PdCl ₂ (PPh ₃) ₂	K ₂ CO ₃	100	13	62
2	PdCl ₂ (PPh ₃) ₂	K ₂ CO ₃	70	13	25
3	PdCl ₂ (PPh ₃) ₂	K ₂ CO ₃	125	13	40
4	PdCl ₂ (PPh ₃) ₂	K ₂ CO ₃	150	13	45
5	PdCl ₂ (PPh ₃) ₂	K ₂ CO ₃	100	20	43
6	PdCl ₂ (PPh ₃) ₂	K ₂ CO ₃	100	6	40
7	PdCl ₂ (PPh ₃) ₂	K ₂ CO ₃	100	1	26
8	PdCl ₂ (PPh ₃) ₂	Et ₃ N	100	13	48
9	PdCl ₂ (PPh ₃) ₂	<i>n</i> -Bu ₃ N	100	13	trace
10	PdCl ₂ (PPh ₃) ₂	DBU	100	13	24
11	PdCl ₂ (PPh ₃) ₂	NaOAc	100	13	16
12	PdCl ₂ (PPh ₃) ₂	KOH	100	13	55
13	PdCl ₂ (MeCN) ₂	K ₂ CO ₃	100	13	trace
14	Pd(OAc) ₂	K ₂ CO ₃	100	13	trace
15	Pd(dba) ₂	K ₂ CO ₃	100	13	16

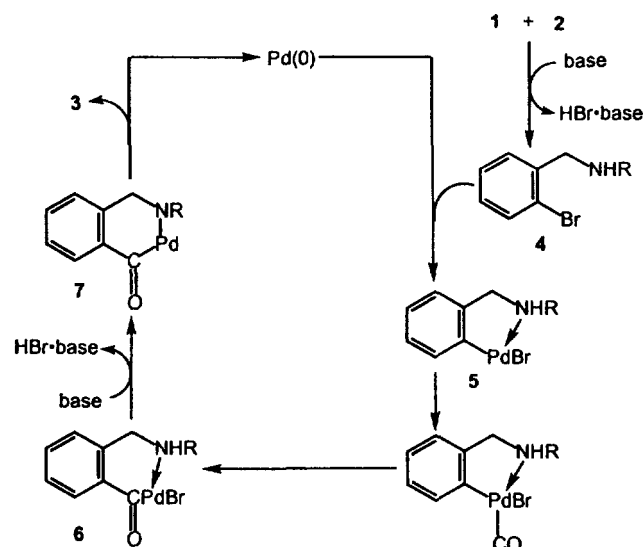
^aAll reactions were carried out with 1 (2 mmol), 2a (2 mmol), palladium salt (0.02 mmol), PPh₃ (0.08 mmol), and base (4 mmol) in DMF (5 mL) for 24 h. ^bIsolated yield.

tion metal-catalyzed carbonylative heterocyclization of *N*-benzyl-*o*-bromobenzylamine with CO to give *N*-benzylisoindolin-1-one, respectively, little is known about the carbonylative heterocyclization of *o*-bromobenzylbromide with primary amines and CO. Thus, treatment of *o*-bromobenzylbromide (1) (2 mmol) with an equimolar amount of aniline (2a) and CO (13 atm) in DMF in the presence of a catalytic amount of bis(triphenylphosphine)palladium(II) chloride (1 mol%), triphenylphosphine (4 mol%), and potassium carbonate (2 mol equiv to 1) at 100 °C for 24 h afforded *N*-phenylisoindolin-1-one (3a) in 62% yield (Scheme 1). This reaction condition was eventually revealed to be the best for obtaining 3a (Table 1, run 1). Both lower and higher reaction temperatures and CO pressures resulted in lower yields of 3a (runs 2-7). A variety of bases, organic and inorganic, can also be used in place of potassium carbonate, but the yield of 3a was generally lower than that by use of potassium carbonate (runs 8-12). The reaction scarcely proceeded using other palladium salts such as PdCl₂(MeCN)₂ and Pd(OAc)₂ in place of PdCl₂(PPh₃)₂ (runs 13 and 14), but Pd(dba)₂ was slightly effective for this heterocyclization (run 15). On the other

Table 2. Palladium-Catalyzed Reactions of *o*-Bromobenzylbromide (1) with Various Amines 2 and CO^a

Run	Amine 2	Product 3	Isolated yield (%)
16	2b	3b	45
17	2c	3c	50
18	2d	3d	35
19 ^b	2e	3e	40
20 ^b	2f	3f	53
21	2g	3g	60
22 ^b	2h	3h	44
23	2i	3i	40

^aAll reactions were carried out with 1 (2 mmol), 2 (2 mmol), PdCl₂(PPh₃)₂ (0.02 mmol), PPh₃ (0.08 mmol), and K₂CO₃ (4 mmol) in DMF (5 mL) at 100 °C for 24 h under CO (13 atm) unless otherwise stated. ^bReaction time (48 h).



Scheme 2.

hand, when this palladium-catalyzed heterocyclization was carried out in the absence of PPh₃, the reaction was retarded (e.g. the yield of 3a decreased from 62 to 40%). This result may indicate that the reduction of Pd(II) to Pd(0) is accelerated by addition of the triphenylphosphine in this reaction system. It has been well known that PPh₃ reduced Pd(OAc)₂ to Pd(0).⁷

From other easily available primary amines 2, the corresponding *N*-substituted isoindolin-1-ones were also formed in good yields. The presence of an electron withdrawing group such as Cl on aromatic ring of the amine 2 lowered the product yield. The yields of the corresponding isoindolin-1-ones were improved by a longer reaction time (runs 19 and 20). Typical results are summarized in Table 2.

The reaction seems to proceed as shown in Scheme 2. Thus, oxidative addition of carbon-bromide bond of *o*-bromobenzylamine 4, initially formed *in situ* by the reaction between 1 and 2, to palladium(0) produces an arylpalladium(II) compound 5, where CO coordination to Pd and then aryl migration from Pd to carbon of CO occurs to produce an aroylpalladium(II) intermediate 6. The elimination of HBr

occurs in the aroylpalladium(II) **6** to give the aroylamidopalladium(II) species **7**. This is followed by reductive elimination to give the corresponding isoindolin-1-ones **3**.⁴²

Experimental Section

General. Commercially available organic and inorganic compounds were used without further purification except for DMF, which was dried by known method. Melting points were measured with a melting point apparatus (Yamato Model MP-21) and were uncorrected. ¹H (300 MHz) and ¹³C (75.5 MHz) NMR spectra were recorded on a Varian Unity Plus 300 spectrometer using Me₄Si as an internal standard in CDCl₃. Chemical shifts are reported in δ units downfield from Me₄Si. IR spectra were recorded on a Mattson Galaxy 6030 (FT) infrared spectrophotometer. Mass spectra were obtained on a Shimadzu GC-MS QP 1000A spectrometer. The thin-layer chromatography plate was prepared with silica gel 60 GF₂₅₄, Merck.

General Procedure for the Synthesis of N-Substituted Isoindolin-1-ones. A mixture of *o*-bromobenzylbromide (0.500 g, 2 mmol), amine (2 mmol), PdCl₂(PPh₃)₂ (0.014 g, 0.02 mmol), PPh₃ (0.020 g, 0.08 mmol), and K₂CO₃ (0.552 g, 4 mmol) in a 100 mL stainless steel autoclave was stirred magnetically in DMF (5 mL) at 100 °C for 24 h under carbon monoxide pressure (13 atm). The reaction mixture was filtered and extracted with chloroform (20 mL×2). The combined organic phase was washed with water and dried over anhydrous MgSO₄. Removal of the solvent under reduced pressure left a crude product which was purified by recrystallization from CHCl₃/diethyl ether or TLC using ethyl acetate/hexane (1/5) mixture as an eluent to give N-substituted isoindolin-1-ones. The products prepared by the above procedure were characterized spectroscopically as shown below.

N-Phenylisoindolin-1-one (3a). 62% yield; a white crystal; mp 161.5-162 °C; IR (KBr) 1667 (C=O) cm⁻¹; ¹H NMR δ 4.80 (s, 2H), 7.15 (t, *J*=7.5 Hz, 1H), 7.30-7.54 (m, 5H), 7.62-7.80 (m, 3H); ¹³C NMR δ 50.6, 119.3, 122.6, 124.0, 124.4, 128.3, 129.1, 132.0, 133.2, 139.4, 140.0, 167.4; MS *m/z* (relative intensity) 209 (M⁺, 100), 181 (56), 104 (41), 77 (22).

N-(*m*-methylphenyl)isoindolin-1-one (3b). 45% yield; a white crystal; mp 144.5-145 °C; IR (KBr) 1690 (C=O) cm⁻¹; ¹H NMR δ 2.41 (s, 3H), 4.23 (s, 2H), 4.85 (s, 2H), 7.01 (d, *J*=7.5 Hz, 1H), 7.48 (m, 5H), 7.72 (s, 1H), 7.94 (d, *J*=8.1 Hz, 1H); ¹³C NMR δ 21.7, 50.9, 116.7, 120.4, 122.6, 124.2, 125.3, 128.3, 128.9, 132.0, 133.4, 139.0, 139.5, 140.2, 167.4; MS *m/z* (relative intensity) 223 (M⁺, 100), 195 (35), 91 (72).

N-(*p*-Methoxyphenyl)isoindolin-1-one (3c). 50% yield; a white crystal; mp 136-137 °C; IR (KBr) 1674 (C=O) cm⁻¹; ¹H NMR δ 3.80 (s, 3H), 4.75 (s, 2H), 6.93 (d, *J*=9.3 Hz, 2H), 7.50 (m, 3H), 7.71 (d, *J*=9.6 Hz, 2H), 7.89 (d, *J*=8.4 Hz, 1H); ¹³C NMR δ 51.0, 55.4, 114.2, 121.3, 122.5, 123.9, 128.2, 131.7, 132.6, 133.2, 140.1, 156.5, 167.1; MS *m/z* (relative intensity) 239 (M⁺, 100), 224 (97), 196 (35), 167 (20).

N-(*m*-Methoxyphenyl)isoindolin-1-one (3d). 35% yield; a white crystal; mp 125-127 °C; IR (KBr) 1690 (C=O) cm⁻¹; ¹H NMR δ 3.85 (s, 3H), 4.81 (s, 2H), 6.73 (m, 1H), 7.31 (m, 2H), 7.51 (m, 3H), 7.67 (s, 1H), 7.90 (d, *J*=8.4 Hz, 1H); ¹³C NMR δ 50.8, 55.3, 105.3, 110.2, 111.2, 122.6, 124.0,

128.3, 129.7, 132.1, 133.2, 140.0, 140.7, 160.2, 167.1; MS *m/z* (relative intensity) 239 (M⁺, 100), 224 (13).

N-(*p*-Chlorophenyl)isoindolin-1-one (3e). 40% yield; a white crystal; mp 177-179 °C; IR (KBr) 1660 (C=O) cm⁻¹; ¹H NMR δ 4.82 (s, 2H), 7.38 (d, *J*=9.0 Hz, 2H), 7.53 (m, 3H), 7.83 (d, *J*=9.0 Hz, 2H), 7.91 (d, *J*=7.2 Hz, 1H); ¹³C NMR δ 50.6, 120.4, 122.6, 124.2, 128.5, 129.1, 132.0, 132.3, 133.0, 138.2, 139.9, 167.5; MS *m/z* (relative intensity) 245 (M⁺+2, 40), 243 (M⁺, 100), 215 (44).

N-(*m*-Chlorophenyl)isoindolin-1-one (3f). 53% yield; a white crystal; mp 185-186 °C; IR (KBr) 1689 (C=O) cm⁻¹; ¹H NMR δ 4.80 (s, 2H), 7.12 (d, *J*=7.8 Hz, 1H), 7.32 (t, *J*=8.1 Hz, 1H), 7.57 (m, 3H), 7.78 (d, *J*=8.1 Hz, 1H), 7.91 (m, 2H); ¹³C NMR δ 50.5, 116.9, 119.1, 122.6, 124.2, 124.3, 128.5, 130.1, 132.4, 132.8, 134.8, 139.8, 140.6, 167.5; MS *m/z* (relative intensity) 245 (M⁺+2, 31), 243 (M⁺, 100), 215 (46).

N-Benzylisoindolin-1-one (3g). 60% yield; a white crystal; mp 88-89 °C (lit.⁴⁴ mp 90-91 °C); IR (KBr) 1662 (C=O) cm⁻¹; ¹H NMR δ 4.24 (s, 2H), 4.78 (s, 2H), 7.28-7.52 (m, 8H), 7.88 (d, *J*=7.8 Hz, 1H); ¹³C NMR δ 46.2, 49.3, 122.6, 123.7, 127.5, 127.9, 128.0, 128.6, 131.2, 132.5, 136.9, 141.1, 168.3; MS *m/z* (relative intensity) 223 (M⁺, 100), 146 (28), 119 (50), 91 (43).

N-(*p*-Methoxybenzyl)isoindolin-1-one (3h). 44% yield; a white crystal; mp 83-85 °C; IR (KBr) 1682 (C=O) cm⁻¹; ¹H NMR δ 3.78 (s, 3H), 4.23 (s, 2H), 4.73 (s, 2H), 6.85 (d, *J*=8.4 Hz, 2H), 7.24 (d, *J*=9.0 Hz, 2H), 7.41 (m, 3H), 7.88 (dd, *J*=6.6 and 1.5 Hz, 1H); ¹³C NMR δ 45.7, 49.2, 55.2, 114.1, 122.6, 123.7, 127.9, 129.1, 129.4, 131.2, 132.7, 141.2, 159.1, 168.3; MS *m/z* (relative intensity) 253 (M⁺, 54), 222 (12), 121 (100).

N-(*n*-Butyl)isoindolin-1-one (3i). 40% yield; a yellow oil; IR (neat) 1678 (C=O) cm⁻¹; ¹H NMR δ 0.97 (t, *J*=3.6 Hz, 3H), 1.37 (m, 2H), 1.65 (m, 2H), 3.62 (t, *J*=7.2 Hz, 2H), 4.37 (s, 2H), 7.43 (m, 3H), 7.84 (d, *J*=8.1 Hz, 1H); MS *m/z* (relative intensity) 189 (M⁺, 26), 146 (100), 118 (10), 91 (28).

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Efficient Synthesis of *hypho*-2,5-S₂B₇H₁₁ and Preparation of New *nido*-, *arachno*-, and *hypho*-Metalladithiaborane Clusters Derived from Its Anion *hypho*-S₂B₇H₁₀⁻

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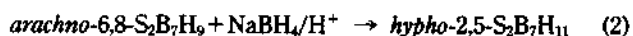
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Reaction of *arachno*-S₂B₇H₈⁻ with either THF or 1,2-dimethoxyethane upon refluxing condition results in the formation of the previously known compound *hypho*-S₂B₇H₁₀⁻. Protonation of *hypho*-S₂B₇H₁₀⁻ with HCl/Et₂O generates *hypho*-2,5-S₂B₇H₁₁ in good yield. This *hypho*-S₂B₇H₁₀⁻ anion has been employed to generate a series of new *nido*-, *arachno*-, and *hypho*-metalladithiaborane clusters. Reaction of the anion with Cp(CO)₂FeCl results in direct metal insertion and the formation of a complex containing the general formula (η⁵-C₅H₅)FeS₂B₇H₈. Spectroscopic studies of *nido*-6-CpFe-7,9-S₂B₇H₈ I demonstrated that compound I was shown to have a *nido*-type cage geometry derived from an octadecahedron missing one vertex, with the iron atom occupying the three-coordinate 6-position in the cage and the two sulfurs occupying positions on the open face of the cage. Reaction of *hypho*-S₂B₇H₁₀⁻ with CoCl₂/Li⁺[C₅H₅]⁻ gave the previously known complex *arachno*-7-CpCo-6,8-S₂B₇H₈ II. Also, the reaction of the anion with [Cp*RhCl₂]₂ gave the complex *arachno*-7-Cp*Rh-6,8-S₂B₇H₈ III, the structure of which was shown to be that of complex II. The similarity of the NMR spectra of II and III suggest that III adopts cage structure similar to that previously confirmed for II. A series of 9-vertex *hypho* clusters in which the sulfur atoms are bridged by different species isoelectronic with a BH₃ unit, such as HMn(CO)₄ or SiR₂ have been prepared. Compounds IV, V, and VI are each 2n+4 skeletal electron systems and would be expected according to skeletal electron counting theory to adopt *hypho*-type polyhedral structures derived from an icosahedron missing three vertices. The complex *hypho*-1-(CO)₄Mn-2,5-S₂B₇H₈ IV was obtained by the reaction of the anion with (CO)₅MnBr and has been shown from spectroscopic data to consist of a (CO)₄Mn fragment bound to the two sulfur atoms S₂ and S₅ of *hypho*-S₂B₇H₁₀⁻. Also, similar *hypho*-type complexes *hypho*-1-R₂Si-2,5-S₂B₇H₈ (R=CH₃ V, R=C₆H₅ VI) have been prepared from the reaction of *hypho*-S₂B₇H₁₀⁻ with R₂SiHCl.

Introduction

Previously *hypho*-2,5-S₂B₇H₁₁ was obtained from either the reaction of BH₃·THF or NaBH₄ with *arachno*-S₂B₇H₈⁻ or *arachno*-6,8-S₂B₇H₉ in moderate yield (24-33%) as shown in equation 1 and 2.^{1,2} The formation of *hypho*-2,5-S₂B₇H₁₁ was viewed as involving an initial interaction between the Lewis acid BH₃ and the base borane anion, followed by a cluster rearrangement.



We recently reported that the reaction of *arachno*-6,8-S₂B₇

H₈⁻ anion with THF or 1,2-dimethoxyethane results in a rearrangement reaction to give good yields (40-47%) of the *hypho*-S₂B₇H₁₀⁻ anion.³ This dithiaborane anion is a rare example of a 2n+8 cluster system (26 skeletal electron, 9 cage atoms) and according to simple skeletal-electron counting theory⁴ should adopt a *hypho* cage geometry based on an icosahedron missing three vertices as shown in Figure 1. When the structures of *hypho*-2,5-S₂B₇H₁₁ and *arachno*-6,8-S₂B₇H₉ are compared, in complex *hypho*-2,5-S₂B₇H₁₁ the electron rich bridging S-BH₂-S unit appears to be connected by conventional two-center, two-electron bonds, whereas the electron deficient six-boron unit adopts a configuration which favors multicenter interactions. Thus, these molecules can