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Palladium-catalyzed C–N bond formation: synthesis of 1-aryl-1*H*-pyrazoles from β-bromovinyl aldehydes and arylhydrazines

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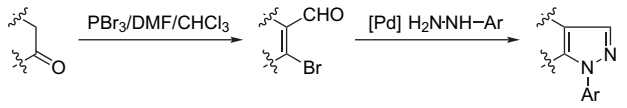
Abstract—Cyclic and acyclic β-bromovinyl aldehydes are cyclized with an array of arylhydrazines in toluene at 125 °C in the presence of a palladium catalyst and a phosphorus chelating ligand together with NaO^{t}Bu to give 1-aryl-1*H*-pyrazoles in moderate to good yields.

1. Introduction

Palladium-catalyzed sp^2-carbon–nitrogen bond forming reaction by the cross-coupling of aryl halides (or triflate) with primary or secondary amines has been recognized as an attractive tool in synthetic organic chemistry.[1] In connection with this report, it is known that several *N*-heterocycles can be synthesized by palladium-catalyzed coupling protocol of aryl halides with hydrazones.[2–9] Buchwald et al. have reported on the synthesis of indoles by palladium-catalyzed coupling of aryl bromides with benzophenone hydrazone followed by the treatment of ketones under $TsOH\cdot H_2O$.[4] Song and Yee have reported a palladium-catalyzed intramolecular amination of *N*-aryl-*N*′-(*o*-bromobenzyl)hydrazines and *N*-aryl-*N*-(*o*-bromobenzyl)hydrazines leading to 1-aryl-1*H*-indazoles and 2-aryl-2*H*-indazoles, respectively.[5,6] It is also reported by Haddad et al. that indazoles can be synthesized by the palladium-catalyzed coupling of aryl halides with benzophenone hydrazone and subsequent reaction with 1,3-bifunctional substrates.[7,8] Such an intrinsic palladium-catalyzed C–N bond formation was also applied to the synthesis of 1-aryl-1*H*-indazoles by us through the coupling between 2-bromobenzaldehydes and arylhydrazines.[9,10] The indazole protocol led us to extend to the reaction with β-bromovinyl aldehydes, which are readily prepared from ketones via the bromo analogue of Vilsmeier reaction (Scheme 1).[11] Herein, this report describes a palladium-catalyzed cyclization of β-bromovinyl aldehydes with arylhydrazines leading to pyrazoles via an intrinsic C–N bond formation.[12,13]



Scheme 1.

2. Results and discussion

Based on our recent report on palladium-catalyzed synthesis of 1-aryl-1*H*-indazoles from 2-bromobenzaldehydes and arylhydrazines,[9] the results of several attempted cyclizations of 2-bromocyclohex-1-enecarbaldehyde (**1a**) with phenylhydrazine (**2a**) are listed in Table 1. Treatment of equimolar amount of **1a** and **2a** in toluene under the catalytic system of $Pd(OAc)_2$ combined with 1,3-bis(diphenylphosphino)propane (dppp) along with NaO^{t}Bu at 100 °C for 24 h afforded 1-phenyl-4,5,6,7-tetrahydro-1*H*-indazole (**3a**) in 34% yield (entry 1). This result indicates that the present reaction, nevertheless the use of more amount of a palladium catalyst, is slower than that of 2-bromobenzaldehyde with **2a** leading to 1-phenyl-1*H*-indazole.[9] Higher reaction temperature resulted in an elevated yield of **3a** (entry 2). Similar catalytic activity was observed with $PdCl_2$ combined with dppp (entry 3). Among the catalytic systems of $Pd(OAc)_2$ combined with mono- and bidentate phosphorus ligands such as PPh_3, 1,1′-bis(diphenylphosphino)ferrocene (dppf), and 1,1′-bis(di-*i*-propylphosphino)ferrocene (dipf) examined dppf revealed to be the ligand of choice and monodentate PPh_3 did not work at all for the present reaction (entries 4–6). On the other hand, when the reaction was carried out under a dilute concentration, **3a** was more effectively formed (entry 7). However, the addition of molecular sieves, 4 Å (0.2 g) under the condition of entry 7 did not give any significant change in

Keywords: β-Bromovinyl aldehydes; C–N bond formation; Arylhydrazines; Palladium catalyst; Pyrazoles.
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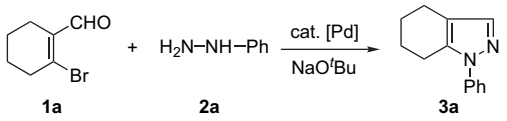
Table 1. Optimization of conditions for the reaction of **1a** with **2a**



1a **2a** **3a**

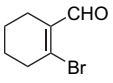
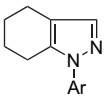
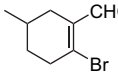
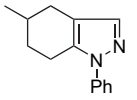
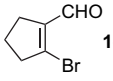
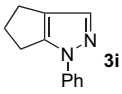
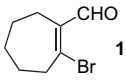
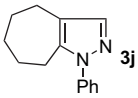
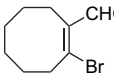
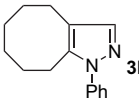
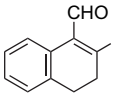
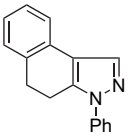
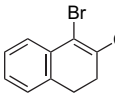
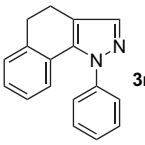
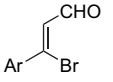
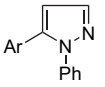
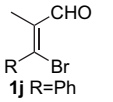
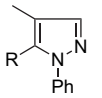
Entry	Ligands	Solvents (mL)	Temperature (°C)	Yield (%)
1	dppp	Toluene (5)	100	34
2	dppp	Toluene (5)	125	59
3[a]	dppp	Toluene (5)	125	57
4	dppf	Toluene (5)	125	67
5	dipf	Toluene (5)	125	60
6	PPh_3	Toluene (5)	125	1
7	dppf	Toluene (10)	125	79
8	(*S*)-(−)-BINAP	Toluene (10)	125	77
9	dppf	THF (10)	125	62
10	dppf	MeCN (10)	125	64

Reaction conditions: **1a** (1 mmol), **2a** (1 mmol), $Pd(OAc)_2$ (0.05 mmol), NaO^{t}Bu (2 mmol), bidentate ligand (0.075 mmol), monodentate ligand (0.15 mmol), for 24 h.
[a] $PdCl_2$ was used in place of $Pd(OAc)_2$.

the yield of **3a** (78%). The catalytic system using (*S*)-(−)-BINAP was revealed to be as effective as that using dppp (entry 8). From the solvents examined THF and MeCN could be alternatively used, but the yield of **3a** was lower than that when toluene was used (entries 9 an 10). As a result, the best result in terms of both yield and complete conversion of **1a** was accomplished by the standard set of reaction conditions shown in entry 7 of Table 1.

Having established reaction conditions, various β-bromovinyl aldehydes **1** were subjected to react with various arylhydrazines **2** in order to investigate the reaction scope and several representative results are summarized in Table 2. Cyclic β-bromovinyl aldehyde **1a** was readily cyclized with an array of arylhydrazines (**2a**–**g**) having electron donating and withdrawing substituents to give the corresponding 1-aryl-1*H*-pyrazoles (**3a**–**g**) in the range of 42–79% yields. The product yield was not significantly affected by the electronic nature of the substituent on the aromatic ring of **2a**–**g**, whereas the position of that had some relevance to the pyrazole yield. With arylhydrazines having *ortho*-substituent, the pyrazole yield was generally lower than that when arylhydrazines having *meta*- and *para*-substituents were used. 2-Bromo-5-methylcyclohex-1-enecarbaldehyde (**1b**) reacts similarly with **2a** to afford 5-methyl-1-phenyl-4,5,6,7-tetrahydro-1*H*-indazole (**3h**) in 76% yield. From the reactions between several cyclic β-bromovinyl aldehydes (**1d** and **1e**) and **2a**, the corresponding pyrazoles (**3j** and **3k**) were produced in similar yields. However, lower reaction yield was observed with five-membered cyclic β-bromovinyl aldehyde **1c**. To test the effect of the position of formyl group and bromide on cyclic β-bromovinyl aldehydes, **1f** and **1g** were employed. However, the cyclization took place similarly irrespective of the position. Next, we carried out the reaction with trans/cis mixture (trans/cis=ca. 1/10 on GLC) of acyclic β-bromovinyl aldehydes (**1h**–**k**), which could not be separated by chromatography.[14] Similar treatment of acyclic β-bromovinyl aldehydes (**1h** and **1i**), which have no substituent at α-position with **2a** under the employed conditions afforded the corresponding 1,5-disubstituted pyrazoles (**3n** and **3o**). Acyclic β-bromovinyl aldehydes such as 3-bromo-2-methyl-3-phenylpropenal (**1j**) and 3-bromo-2-methylpent-2-enal (**1k**), which have a substituent at α-position were also reacted with **2a** to give 4-methyl-1,5-dimethyl-1*H*-pyrazole (**3p**) and 5-ethyl-4-methyl-1-phenyl-1*H*-pyrazole (**3q**) in 56 and 40% yields, respectively.

Table 2. Palladium-catalyzed synthesis of 1-aryl-1*H*-pyrazoles

β-Bromovinyl aldehyde **1**	Arylhydrazine **2**	Product **3**	Yield (%)
 **1a**	H_2N–NH–Ar	 **3a**	
	2a Ar=Ph		79
	2b Ar=2-MeC_6H_4	**3b**	42
	2c Ar=3-MeC_6H_4	**3c**	56
	2d Ar=4-MeC_6H_4	**3d**	68
	2e Ar=4-$MeOC_6H_4$	**3e**	54
	2f Ar=2-$CF_3C_6H_4$	**3f**	45
	2g Ar=4-$NO_2C_6H_4$	**3g**	56
 **1b**	**2a**	 **3h**	76
 **1c**	**2a**	 **3i**	20
 **1d**	**2a**	 **3j**	65
 **1e**	**2a**	 **3k**	77
 **1f**	**2a**	 **3l**	54
 **1g**	**2a**	 **3m**	46
 **1h** Ar=Ph	**2a**	 **3n**	48
1i Ar=2-naphthyl	**2a**	**3o**	48
 **1j** R=Ph	**2a**	 **3p**	56
1k R=Et	**2a**	**3q**	40

Reaction conditions: **1** (1 mmol), **2** (1 mmol), $Pd(OAc)_2$ (5 mol %), dppf (7.5 mol %), NaO^{t}Bu (2 mmol), toluene (10 mL), 125 °C, for 24 h.

In summary, we have demonstrated that cyclic and acyclic β-bromovinyl aldehydes are cyclized with an array of arylhydrazines in the presence of a palladium catalyst and a phosphorus chelating ligand to afford pyrazoles via an

intrinsic C–N bond protocol. The present reaction is a new route for the synthesis of pyrazoles from ketones.

3. Experimental

3.1. General

^{1}H and ^{13}C NMR (400 and 100 MHz) spectra were recorded on a Bruker Avance Digital 400 spectrometer using TMS as an internal standard. Melting points were determined on a Thomas–Hoover capillary melting point apparatus and were uncorrected. The isolation of pure products was carried out via thin layer (silica gel 60 GF_{254}, Merck) chromatography. β-Bromovinyl aldehydes **1** were prepared by the reported methods.[11] Commercially available organic and inorganic compounds were used without further purification except for toluene, THF, and MeCN, which were distilled by known methods before use.

3.2. Typical procedure for palladium-catalyzed synthesis of pyrazoles from β-bromovinyl aldehydes and arylhydrazines

A mixture of 2-bromocyclohex-1-enecarbaldehyde (**1a**) (0.189 g, 1 mmol), phenylhydrazine (**2a**) (0.108 g, 1 mmol), $Pd(OAc)_2$ (0.011 g, 0.05 mmol), dppf (0.042 g, 0.075 mmol), and NaO^{t}Bu (0.192 g, 2 mmol) in toluene (10 mL) was placed in a 50 mL pressure vessel. After the system was flushed with argon, the mixture was stirred at 125 °C for 24 h. The reaction mixture was passed through a short silica gel column (ethyl acetate) to eliminate inorganic salts. Removal of the solvent left a crude mixture, which was separated by thin layer chromatography (silica gel, ethyl acetate/hexane=1/10) to give 1-phenyl-4,5,6,7-tetrahydro-1*H*-indazole (**3a**) (0.157 g, 79%). All new compounds prepared by the above procedure were characterized spectroscopically as shown below.

3.2.1. 1-(2-Methylphenyl)-4,5,6,7-tetrahydro-1*H*-indazole (3b). Oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.75–1.80 (m, 4H), 2.08 (s, 3H), 2.35–2.37 (m, 2H), 2.58–2.60 (m, 2H), 7.23–7.34 (m, 4H), 7.44 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.44, 20.68, 21.90, 22.88, 23.14, 115.95, 126.29, 127.43, 128.71, 130.93, 135.97, 137.90, 138.74, 139.29; Anal. Calcd for $C_{14}H_{16}N_2$: C 79.21; H 7.60; N 13.20; found: C 79.04; H 7.88; N 13.00.

3.2.2. 1-(3-Methylphenyl)-4,5,6,7-tetrahydro-1*H*-indazole (3c). Oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.74–1.82 (m, 4H), 2.39 (s, 3H), 2.56–2.59 (m, 2H), 2.70–2.72 (m, 2H), 7.10 (d, J=7.5 Hz, 1H), 7.24–7.34 (m, 3H), 7.45 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.14, 21.80, 23.22, 23.57, 24.08, 118.00, 120.33, 124.25, 127.76, 129.10, 138.54, 139.03, 139.49, 140.43; Anal. Calcd for $C_{14}H_{16}N_2$: C 79.21; H 7.60; N 13.20; found: C 78.98; H 7.85; N 13.13.

3.2.3. 1-(4-Methylphenyl)-4,5,6,7-tetrahydro-1*H*-indazole (3d). Oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.74–1.82 (m, 4H), 2.37 (s, 3H), 2.56–2.59 (m, 2H), 2.67–2.70 (m, 2H), 7.22 (d, J=8.0 Hz, 2H), 7.34–7.38 (m, 2H), 7.44 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.74, 20.99, 22.84, 23.16, 23.55, 117.45, 122.99, 129.56, 136.43, 137.70, 138.11, 138.47; Anal. Calcd for $C_{14}H_{16}N_2$: C 79.21; H 7.60; N 13.20; found: C 79.08; H 7.81; N 13.06.

3.2.4. 1-(4-Methoxyphenyl)-4,5,6,7-tetrahydro-1*H*-indazole (3e). Oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.74–1.86 (m, 4H), 2.56–2.59 (m, 2H), 2.64–2.67 (m, 2H), 3.83 (s, 3H), 6.93–6.97 (m, 2H), 7.36–7.40 (m, 2H), 7.42 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.12, 23.26, 23.50, 23.69, 55.90, 114.54, 117.58, 125.10, 133.79, 138.56, 138.63, 158.73; Anal. Calcd for $C_{14}H_{16}N_2O$: C 73.66; H 7.06; N 12.27; found: C 73.51; H 7.31; N 12.24.

3.2.5. 1-(2-Trifluoromethylphenyl)-4,5,6,7-tetrahydro-1*H*-indazole (3f). Oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.72–1.81 (m, 4H), 2.33–2.36 (m, 2H), 2.57–2.59 (m, 2H), 7.34 (d, J=7.5 Hz, 1H), 7.46 (s, 1H), 7.57 (t, J=7.5 Hz, 1H), 7.62–7.66 (m, 1H), 7.79–7.81 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.92, 21.98, 23.09, 23.36, 116.73, 123.31 (q, J=272.4 Hz), 127.72 (q, J=4.8 Hz), 128.68 (q, J=31.2 Hz), 129.65, 130.56, 132.87, 138.01 (q, J=1.9 Hz), 139.01, 140.82; Anal. Calcd for $C_{14}H_{13}F_3N_2$: C 63.15; H 4.92; N 10.52; found: C 63.41; H 5.04; N 10.54.

3.2.6. 1-Phenyl-1,4,5,6-tetrahydrocyclopentapyrazole (3i). Oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.57–2.69 (m, 4H), 2.97–3.01 (m, 2H), 7.20–7.24 (m, 1H), 7.38 (s, 1H), 7.39–7.43 (m, 2H), 7.62–7.65 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.15, 26.85, 31.37, 119.41, 125.98, 129.64, 129.74, 135.20, 140.88, 148.90; Anal. Calcd for $C_{12}H_{12}N_2$: C 78.23; H 6.57; N 15.21; found: C 77.91; H 6.81; N 15.06.

3.2.7. 1-Phenyl-1,4,5,6,7,8-hexahydrocycloheptapyrazole (3j). Solid (hexane/chloroform); mp 90 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.61–1.72 (m, 4H), 1.82–1.87 (m, 2H), 2.61–2.64 (m, 2H), 2.75–2.78 (m, 2H), 7.33–7.38 (m, 4H), 7.43–7.46 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.05, 27.58, 27.63, 28.94, 32.23, 122.37, 125.86, 127.83, 129.30, 140.12, 140.41, 142.54; Anal. Calcd for $C_{14}H_{16}N_2$: C 79.21; H 7.60; N 13.20; found: C 79.22; H 7.72; N 12.99.

3.2.8. 1-Phenyl-4,5,6,7,8,9-hexahydro-1*H*-cyclooctapyrazole (3k). Oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.46–1.55 (m, 4H), 1.64–1.73 (m, 4H), 2.61–2.64 (m, 2H), 2.72–2.75 (m, 2H), 7.34–7.47 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.90, 23.52, 25.42, 25.71, 28.87, 30.44, 119.71, 125.25, 127.54, 128.96, 139.59, 140.18, 140.36; Anal. Calcd for $C_{15}H_{18}N_2$: C 79.61; H 8.02; N 12.38; found: C 79.40; H 8.16; N 12.22.

3.2.9. 5-Naphthalen-2-yl-1-phenyl-1*H*-pyrazole (3o). Oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.60 (d, J=1.5 Hz, 1H), 7.22–7.34 (m, 6H), 7.45–7.50 (m, 2H), 7.70–7.80 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 108.62, 125.59 (×2), 126.75, 126.94, 127.05, 127.85, 128.11, 128.34, 128.46, 128.57, 129.36, 133.17, 133.50, 140.59, 140.83, 143.37; Anal. Calcd for $C_{19}H_{14}N_2$: C 84.42; H 5.22; N 10.36; found: C 84.54; H 5.33; N 9.91.

3.2.10. 5-Ethyl-4-methyl-1-phenyl-1*H*-pyrazole (3q). Oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28 (t, J=7.5 Hz, 3H), 2.08

(s, 3H), 2.67 (q, J=7.5 Hz, 2H), 7.17–7.20 (m, 1H), 7.37–7.41 (m, 2H), 7.60–7.62 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 8.47, 13.47, 20.06, 115.84, 118.40, 125.35, 125.81, 129.27, 140.35, 154.99; Anal. Calcd for $C_{12}H_{14}N_2$: C 77.38; H 7.58; N 15.04; found: C 77.00; H 7.88; N 14.94.

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