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Palladium-Catalyzed Stereoselective Reductive Coupling Reactions of Organic Halides with 7-Heteroatom Norbornadienes

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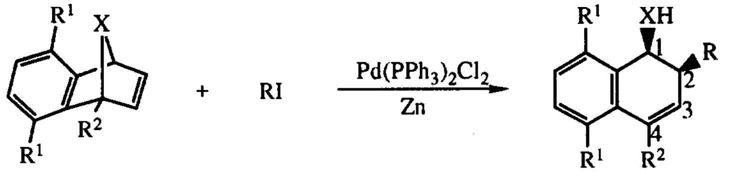
Abstract: Organic halides react with 7-heteroatom benzonorbornadiene derivatives **1** - **4** in the presence of $Pd(PPh_3)_2Cl_2$ and zinc powder to give *cis*-1,2-dihydro-1-naphthol or methyl N-(*cis*-1,2-dihydro-1-naphthyl) carbamate derivatives stereoselectively.

Oxidation of organic substrates mediated by palladium complexes in the presence of suitable oxidants are well known due to the high oxidizing ability of palladium(II) species.[1] The use of palladium complexes accompanied by reducing agents for organic reactions are much less studied.[2] Recently, we successfully employed $Pd(PPh_3)_2Cl_2$ with zinc metal as the reductant for the catalytic reactions of aryl iodides with norbornadiene to give aryl substituted nortricyclenes.[3] The results prompt us to investigate the addition reaction of organic halides with the closely related 7-heteroatom benzonorbornadiene derivatives. This palladium-catalyzed reaction provides a novel method for preparing a series of *cis*-1,2-dihydro-1-naphthol and methyl N-(*cis*-1,2-dihydro-1-naphthyl)carbamate derivatives steroselectively. (eq. 1).

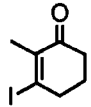
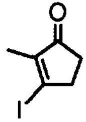
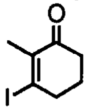


(1)

1: X = O, $R^1 = R^2 = H$	**5**
2: X = O, $R^1 = OCH_3$, $R^2 = H$	**6**
3: X = O, $R^1 = OCH_3$, $R^2 = CH_3$	**7**
4: X = NCO_2Me, $R^1 = R^2 = H$	**8**

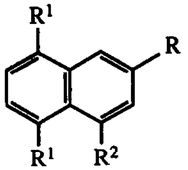
A typical example for the catalytic addition of organic halides to 7-heteroatom benzonorbornadiene derivatives is as follows. To a solution consisting of **1** (1.50 mmole), *p* -$CH_3OC_6H_4I$ (1.00 mmole), and Et_3N (8.0 mmole) in THF (20 mL) were added $Pd(PPh_3)_2Cl_2$ (0.02 mmole), zinc powder (10.0 mmole), and zinc chloride (0.5 mmole). The mixture was heated at 60 °C for 6 h and then separated on silica gel column using ethyl acetate/*n*-hexane as the eluent to give the corresponding *cis* -1,2-dihydro-1-naphthol derivative **5a** in 95% yield. Control reactions indicate that in the absence of Pd species, no desired product was observed, while the omission of zinc afforded only a trace of the expected product. In addition, the omission of either zinc chloride or triethylamine greatly decreased the yield of the desired product.

Table 1. The Addition of Organic Halides to 7-Heteroatom Benzonorbornadiene.

entry	substrate	organic halide	reaction time (h)	products	isolated yield (%)
1	**1**	p - $CH_3OC_6H_4I$	6	**5a**	95
2	**1**	m - $CH_3C_6H_4I$	8	**5b**	95
3	**1**	C_6H_5I	4	**5c**	86
4	**1**	o - $CH_3C_6H_4I$	11	**5d**	98
5	**1**	p - HOC_6H_4I	8	**5e**	94
6	**1**	1-iodonaphthalene	10	**5f**	94
7	**1**	p - $CH_3COC_6H_4I$	13	**5g**	10[a]
8[b]	**1**	2-iodothiophene	37	**5h**	71
9[b]	**1**	$C_6H_5CH_2Br$	11	**5i**	99
10	**1**		9	**5j**	83
11	**1**		6	--	0[c]
12	**2**	m - $CH_3OC_6H_4I$	10	**6a**	94
13	**2**		12	**6b**	71
14	**3**	p - $CH_3OC_6H_4I$	10	**7**	85
15	**4**	p - $CH_3OC_6H_4I$	11	**8a**	87[d]
16	**4**	p - $CH_3C_6H_4I$	8	**8b**	80

a. Major product is 2-(4-acetylphenyl)naphthalene with yield of 70%. *b.* NEt_3 was not added to the catalytic reaction system. *c.* Major product is 2-methyl-3-(2-naphthyl)-2-cyclopenten-1-one with yield of 81%. *d.* The yield was determined by NMR using an internal standard.

As shown in Table 1, various aryl iodides, iodothiophene, benzyl bromide, and 3-iodo-2-methyl-2-cyclohexen-1-one all react with **1** to give high yields of the expected products **5**. All these products exhibit characteristic proton resonances in the range 2.5-7.0 ppm for the two olefinic protons and the protons attached to C-1 and C-2. For example, the corresponding olefinic resonances of product **5a**[4] appear at δ 6.13 (H-3, dd) and 6.70 (H-4, dd), while the resonances of H-1 and H-2 come at δ 4.95 and 3.83, respectively. Week coupling (1.8 Hz) between H-2 and H-4 was detected. The presence of a hydroxyl group was evidenced by the observation of a broad resonance at δ 1.64, while the cis stereochemistry of the hydroxyl and the aryl substituents was established based on the proton-proton coupling constant of 6.0 Hz between H_1 and H_2.[5] The result of an X-ray structure determination of **8b** (Table 1) indicating a cis arrangement of the tolyl and the carbamate groups[6] further supports the proposed structure. For aryl iodide bearing an electron-withdrawing substituent, the corresponding substituted naphthalene **9** derivative was observed as the major product. In general, a few percent of 1-naphthol **10** was also isolated from the reaction mixture. This side product increases as the concentration of zinc halide used increases. In addition to **1**, substrates **2**[7] and **3** also react with aryl halides to afford the expected *cis* -1,2-dihydro-1-naphthol derivatives **6** and **7**. It is worth to mention that the addition of aryl group to **3** occurs regioselectively at the double-bond carbon distal to the methyl group to give product **7**.



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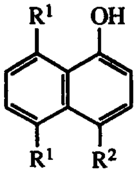

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The observed *cis* -1,2-dihydro-1-naphthol derivative may be considered as a trans addition product of a water molecule to 2-substituted naphthalenes. Due to the great stability of the latter two compounds, the dehydration of *cis* -1,2-dihydro-1-naphthol is expected to be a thermodynamically favorable process. Indeed, all the products **5** readily undergo dehydration in the presence of acid to give the corresponding substituted naphthalenes in essentially quantitative yields. However, in basic or neutral solution, **5** is stable to more than 100 °C.

Under similar catalytic conditions for the formation of **5**, organic halides also react with 7-azabenzonorbornadiene (**4**)[8] to afford methyl N-(*cis*-1,2-dihydro-1-naphthyl)carbamate derivatives **8** (Table 1).[9] The corresponding naphthalene derivatives from deamination of **8** was often observed as a minor product. The compound **8** is also thermodynamically unstable undergoing deamination to afford the corresponding naphthalene derivative in the presence of acid.

Based on the observed reaction products and the known chemistry of the insertion of norbornadiene to aryl-Pd bond, the mechanism for the present catalysis is expected to involved oxidation addition of RI to Pd(0) species to yield $Pd(PPh_3)_2RI$, exo addition of R-Pd to substrate **1** followed by β-heteroatom elimination and then protonation[10] of the latter species affords **5** and a Pd(II) species. The reduction of the Pd(II) species by Zn metal to Pd(0) completes the catalytic cycle. The proposed exo addition gains strong support from the observation that reaction of $Pd(PPh_3)_2ArI$ with norbornadiene yields a Pd complex in which the aryl group and the Pd center are all at the exo positions.[3]

We have demonstrated a convenient method for the preparation of a series of *cis*-1,2-dihydro-1-naphthol and methyl N-(*cis*-1,2-dihydro-1-naphthyl)carbamate derivatives. The presence of hydroxyl and alkene group in these compounds appears useful for further functional group transformation. Studies on the application of these products in organic synthesis are underway.

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4. Selected spectral data (**5a**): ^1H NMR (400MHz, $CDCl_3$, 25 °C): δ 1.64 (br. s, O*H*, 1 H), 3.80 (s, $OC\mathit{H}_3$, 3 H), 3.83 (ddd, J = 6.0 Hz, J = 4.0 Hz, J = 2.0 Hz, *H*(2), 1 H), 4.95 (br., *H*(1), 1 H), 6.13 (dd, J = 9.6 Hz, J = 4.4 Hz, *H*(3), 1 H), 6.70 (dd, J = 9.4 Hz, J = 1.8 Hz, *H*(4), 1 H), 6.86 (d, J = 8.6 Hz, 2 H), 7.18 (d, J = 8.6 Hz, 2 H + 1 H), 7.25-7.38 (m, 3 H); $^{13}C\ \{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): δ 46.26, 55.09 ($O\mathit{C}H_3$), 71.14, 113.93, 126.15, 126.38, 127.87, 128.03, 129.06, 130.02, 130.20, 132.59, 136.17, 158.81; IR (CH_2Cl_2): 3452, 3060, 3036, 2944, 2897, 2836, 1693, 1603, 1511, 1302, 1258, 1179, 1032, 837, 806 cm^{-1}; HRMS calcd for $C_{17}H_{16}O_2$ 252.1151. found 252.1149.
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9. Selected spectral data (**8a**): ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 3.68 (s, $OC\mathit{H}_3$, 3 H), 3.77 (s, $OC\mathit{H}_3$, 3 H), 3.81-3.84 (m, *H*(2), 1 H), 4.71 (d, N*H*, J = 10.0 Hz, 1 H), 5.37 (t, J = 8.6 Hz, *H*(1), 1 H), 6.15 (dd, J = 9.8 Hz, J = 5.3 Hz, *H*(3), 1 H), 6.69 (d, J = 9.8 Hz, *H*(4), 1 H), 6.78 (d, J = 8.6 Hz, 2 H), 7.02 (d, J = 8.7 Hz, 2 H), 7.16-7.29 (m, 4 H); $^{13}C\{^1H\}$ NMR(100 MHz, $CDCl_3$, 25 °C): 43.83, 52.12 ($O\mathit{C}H_3$), 52.75, 55.03 ($O\mathit{C}H_3$), 113.81, 125.13, 126.21, 127.60, 127.90, 127.96, 128.69, 129.89, 130.50, 133.20, 134.41, 156.59 (*C*OO), 158.81; IR (KBr): 3386, 3040, 2992, 2894, 1723, 1605, 1516, 1331, 1235, 1169, 1034, 873, 832, 778, 756, 695 cm^{-1}; HRMS: calcd for $C_{19}H_{19}NO_3$ 309.1366 found 309.1354; mp 126 °C dec.; Anal. calcd for $C_{19}H_{19}NO_3$: C, 73.77; H, 6.19; N, 4.53. found: C, 73.02; H, 6.19; N, 4.46.
10. A possible proton source is from the water containing in the $ZnCl_2$ salt which was not dried prior to use. In the absence of $ZnCl_2$, extra water is necessary to proceed the catalytic reaction .

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