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# PALLADIUM-CATALYZED ARYLATION OF ALLYLIC ALCOHOLS WITH ARYL IODIDES IN WATER

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## PALLADIUM-CATALYZED ARYLATION OF ALLYLIC ALCOHOLS WITH ARYL IODIDES IN WATER

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#### ABSTRACT

Palladium-catalyzed arylation of allylic alcohols with aryl iodides are shown to occur in the presence of sodium bicarbonate and *tetra-n*-butylammonium chloride in pure water using palladium acetate as catalyst.  $\beta$ -aromatic carbonyl compounds are obtained in good yields.

The formation of a carbon-carbon bond by palladium-catalyzed coupling of aryl or vinyl halides with olefins, known as the Heck reaction, has become a powerful tool in organic chemistry.<sup>1</sup> In the case of allylic alcohols, palladium-catalyzed reaction of aryl halides usually affords  $\beta$ -aromatic carbonyl compounds.<sup>2</sup> Jeffery<sup>3</sup> reported that in the presence of sodium bicarbonate and *tetra-n*-butylammonium chloride, a highly selective formation of

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 $\beta$ -aromatic carbonyl compounds can be achieved using palladium acetate as catalyst, the reaction being performed in *N*,*N*-dimethylformamide. The Heck reactions are usually carried out in anhydrous organic solvents.<sup>1a</sup>

The use of water as a reaction medium for transition metal catalyzed reactions is very attractive for organic synthesis,<sup>4</sup> for both economic and safety reasons. Bumagin et al<sup>5</sup> investigated the carbonylation of aryl iodides, the coupling reactions of aryl halides with boronic acids and the arylation of water insoluble olefins in neat water in the presence of palladium salts PdX<sub>2</sub>. The reactions proceeded, under mild conditions, with high rates and good yields. Here we wish to report the palladium-catalyzed arylation of allylic alcohols with aryl iodides in neat water without any organic co-solvent (Scheme 1), a highly selective formation of  $\beta$ -aromatic carbonyl compounds can be achieved.



Treatment of 3-buten-2-ol (3 mmol) with iodobenzene (1 mmol) in neat water (3 ml) at 80°C for 20 h in the presence of a catalytic amount of Pd(OAc)<sub>2</sub> (0.02 mmol), sodium bicarbonate (2.5 mmol) and tetra-n-butylammonium chloride (0.1 mmol) afforded 4-phenyl-2-butanone in a 87% yield. The arylation of 3-buten-2-ol with substituted iodobenzene also proceeded smoothly in water under the same conditions and a variety of 4-aryl-2butanones were obtained in good vields. The results are summarized in Table 1. 4-Aryl-2-butanones all showed strong IR bands at about 1710 cm<sup>-1</sup>, and their <sup>1</sup>H NMR spectra were consistent with the proposed structures. The arylation reaction of 3-buten-2-ol with bromobenzene in water in the presence of a catalytic amount of  $Pd(OAc)_2$  and  $PPh_3$  was slow and a mixture of 4-phenyl-2-butanone (32%) and 4-phenyl-3-buten-2ol (48%) was formed after 48 h. A similar observation has been made by Heck<sup>2a</sup> using triethylamine as the base.

This method was applicable to the arylation of 2-propen-1-ol and 2-methyl-2-propen-1-ol with aryl iodides in neat water and a variety of 3-arylaldehydes were obtained in good yields. These results are also shown in Table 1. 3-Arylaldehydes all showed strong IR bands at about  $1720 \text{ cm}^{-1}$ , and their <sup>1</sup>H NMR spectra were consistent with the proposed

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#### ALLYLIC ALCOHOLS

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*Table 1.* Palladium-Catalyzed Arylation of Allylic Alcohols with Aryl Iodides in Neat Water<sup>a</sup>

Entry	Aryl Iodide	Allylic Alcohol	t/h	Product (Yield, %) <sup>b</sup>
1	C <sub>6</sub> H <sub>5</sub> I	CH2=CHCH(OH)CH3	20	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub>
				$C(O)CH_{3}(87)$
2	4-ClC <sub>6</sub> H <sub>4</sub> I	CH2=CHCH(OH)CH3	17	4-ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> CH <sub>2</sub>
				$C(O)CH_{3}(84)$
3	$4-CH_3OC_6H_4I$	CH <sub>2</sub> =CHCH(OH)CH <sub>3</sub>	24	$4-CH_3OC_6H_4CH_2$
				$CH_2C(O)CH_3(86)$
4	$4-CH_3C_6H_4I$	CH2=CHCH(OH)CH3	22	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> CH <sub>2</sub>
				C(O)CH <sub>3</sub> (80)
5	C <sub>6</sub> H <sub>5</sub> I	CH2=CHCH2OH	20	$C_6H_5CH_2CH_2$
				CHO(85)
6	4-ClC <sub>6</sub> H <sub>4</sub> I	CH2=CHCH2OH	18	4-ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> CH <sub>2</sub>
				CHO(82)
7	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> I	CH2=CHCH2OH	24	$4-CH_3OC_6H_4CH_2$
				$CH_2CHO(84)$
8	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> I	CH2=CHCH2OH	23	$4-CH_3C_6H_4CH_2$
				$CH_2CHO(79)$
9	C <sub>6</sub> H <sub>5</sub> I	CH2=C(CH3)CH2OH	20	$C_6H_5CH_2CH(CH_3)$
				CHO(81)
10	4-ClC <sub>6</sub> H <sub>4</sub> I	CH2=C(CH3)CH2OH	17	4-ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )
				CHO(83)
11	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> I	CH2=C(CH3)CH2OH	23	$4-CH_3OC_6H_4CH_2$
				CH(CH <sub>3</sub> )CHO(80)
12	$4-CH_3C_6H_4I$	CH2=C(CH3)CH2OH	21	4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )
				CHO(75)

<sup>a</sup>Reactions were carried out at  $80^{\circ}$ C with 1 mmol of aryl iodide, 3 mmol of allylic alcohol, 0.02 mmol of Pd(OAc)<sub>2</sub>, 2.5 mmol of NaHCO<sub>3</sub>, and 0.1 mmol of Bu<sub>4</sub>NCl in 3 ml of H<sub>2</sub>O.

<sup>b</sup>Yields are of isolated, pure products and based on the aryl iodides.

structures. As seen from the Table 1, there is no noticeable difference in reactivity between iodobenzenes having electron-withdrawing groups and iodobenzenes having electron-donating groups.

The arylation reaction is highly regioselective with respect to the addition of the aromatic group, only  $\beta$ -substitution is observed. The structural isomer selectivity is also very high, only traces of  $\beta$ -aromatic  $\alpha$ , $\beta$ -unsaturated alcohol compounds are obtained. But in the presence of sodium carbonate instead of sodium bicarbonate, the arylation reaction of allylic alcohols with aryl iodides afforded  $\beta$ -aromatic carbonyl

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compounds as the main products together with a considerable amounts of  $\beta$ -aromatic  $\alpha$ ,  $\beta$ -unsaturated alcohol compounds.

In conclusion, the palladium-catalyzed arylation of allylic alcohols with aryl iodides in neat water described here has not only high regioselectivity and structural isomer selectivity, but offers advantages of being a simple and practical procedure, carried out under mild reaction conditions and giving good yields.

#### **EXPERIMENTAL**

IR spectra were obtained using a Shimadzu IR-435 grating spectraphotometer. <sup>1</sup>H NMR spectra were recorded on a JEOL FX-90Q(90 MHz) instrument with TMS as an internal standard in  $CCl_4$  or  $CDCl_3$  as solvent. All reagents were used as received without further purification.

#### Typical Procedure: Synthesis of 4-phenyl-2-butanone

To a 50 ml round-bottomed flask, fitted with a magnetic stirrer bar and a reflux condensor, were placed Pd(OAc)<sub>2</sub> (4 mg, 0.02 mmol), iodobenzene (0.204 g, 1 mmol), 3-buten-2-ol (0.216 g, 3 mmol), NaHCO<sub>3</sub> (0.210 g, 2.5 mmol), Bu<sub>4</sub>NCl (28 mg, 0.1 mmol), and H<sub>2</sub>O (3 ml). The mixture was stirred vigorously at 80°C for 20 h under nitrogen. The reaction mixture was cooled and dissolved in diethyl ether (50 ml). The ethereal solution was washed with water ( $4 \times 30$  ml), dried over anhydrous MgSO<sub>4</sub>, and then concentrated under reduced pressure. The residue was purified by preparative TLC on silica gel (light petroleum : ethyl acetate = 8:1) to afford 0.129 g (87% yield) of 4-phenyl-2-butanone.

#### ACKNOWLEDGMENT

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