SHORT PAPER

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Palladium-catalysed arylation of butyl acrylate and acrylamide with aryl Iodides in water[†]

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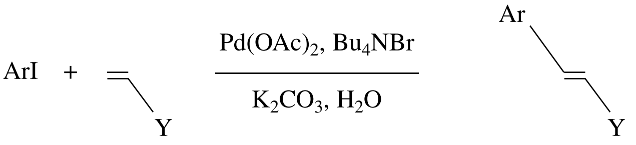
The Heck arylation of butyl acrylate and acrylamide with aryl iodides in the presence of catalytic amounts of palladium acetate and tetra-*n*-butylammonium bromide in pure water using potassium carbonate as base gave the corresponding substituted (*E*)-butyl cinnamates and (*E*)-cinnamamides in good yields, respectively.

Keywords: palladium catalysis, butyl acrylate, acrylamide

The palladium-catalysed arylation of alkenes was an important discovery in organopalladium chemistry made by Heck and coworkers. and has found wide application in organic synthesis.[1,2] The Heck arylation reaction is usually carried out in anhydrous organic solvent.[3] The use of water as a reaction medium for transition metal catalysed reactions is very attractive for organic synthesis,[4–9] for both economic and safety reasons. The arylation of olefins has been shown to proceed very smoothly in a aqueous-organic media in the presence of $Pd(OAc)_2$.[10–12] Water soluble olefins can react with soluble aryl iodides in pure water in the presence of simple palladium salts.[13] Recently, Bumagin *et al.* reported the palladium-catalysed arylation of styrene and acrylic acid in neat water.[14] Jeffery reported arylation reaction of methyl acrylate with iodobenzene in water,[15] the reaction using one equivalent of quaternary ammonium salt as phase transfer catalyst

The arylation of methyl acrylate with substituted iodobenzenes has not been investigated. To our knowledge, no palladium-catalysed arylation of acrylamide with aryl halides in water has been reported. In this paper we report the palladium-catalysed arylation of butyl acrylate and acrylamide with aryl iodides in the presence of catalytic amounts of $Pd(OAc)_2$ and Bu_4NBr in pure water without any organic co-solvents (Scheme 1).



Scheme 1 Y = $CO_2Bu \equiv n - Bu$; $CONH_2$

Treatment of iodobenzene (1 mmol) with butyl acrylate (2 mmol) in neat water (2.5 ml) at 90°C for 6 h in the presence of K_2CO_3 (1.5mmol), Bu_4NBr (0.1 mmol) and a catalytic amount of $Pd(OAc)_2$ (0.02 mmol) afforded (*E*)-butyl cinnamate in 79% yield. However, arylation of butyl acrylate with iodobenzene in water under conditions reported by Jeffery[15] gave only 24% (*E*)-butyl cinnamate. We applied the new reaction to various substituted iodobenzenes, typical results are summarised in Table 1. As seen from the Table 1, the arylation of butyl acrylate with substituted iodobenzenes in neat water also proceeded smoothly and a variety of substituted (*E*)-butyl cinnamates were obtained in good yields. The reactivity of iodobenzenes having electron-withdrawing substituents was higher than that of iodobenzenes having electron-donating substituents. The arylation reaction of aryl bromides with butyl acrylate in neat water under similar conditions was slow, *e.g.* the reaction of 4-bromochlorobenzene and butyl acrylate occured in the presence of K_2CO_3, 10mol% Bu_4NBr and a catalytic amount of $Pd(PPh_3)_2Cl_2$ (2 mol%) in neat water to give after 10h only 21% (E)-butyl 4-chlorocinnamate.

The arylation reaction of aryl iodides with acrylamide in neat water also readily took place in the presence of K_2CO_3, 10 mol% Bu_4NBr and a catalytic amount of $Pd(OAc)_2$ (2 mol%). The results are also summarised in Table 1. As is evident, a variety of substituted (*E*)-cinnamamides can be successfully prepared by treating substituted iodobenzenes with acrylamide in water. However, the reactivity of aryl bromides was poor and only trace products were obtained. Products in Table 1 gave satisfactory m.p.s. and IR and ^1H NMR spectra where comparison was possible. Amalgamated data are included in other cases.

In conclusion, the palladium-catalysed arylation of butyl acrylate and acrylamide with aryl iodides in neat water provides a practical procedure for the stereo-selective synthesis of substituted (*E*)-butyl cinnamates and (*E*)-cinnamamides.

Experimental

M.p.s are uncorrected. IR spectra were obtained on a Shimadzu IR-435 instrument. ^1H NMR spectra were recorded on a JEOL FX-90Q (90 MHz) instrument with Me_4Si as an internal standard in $CDCl_3$ or DMSO-d_6 as solvent. Butyl acrylate was distilled before use, other reagents were used as received without further purification.

Typical procedure for the synthesis of (*E*)-butyl cinnamates

A mixture of butyl acrylate (2 mmol), iodobenzene (1 mmol), $Pd(OAc)_2$ (0.02 mmol), Bu_4NBr (0.1 mmol) and K_2CO_3 (1.5 mmol) in H_2O (2.5 ml) was stirred vigorously under nitrogen at 90°C for 6 h. The reaction mixture was cooled and extracted with diethyl ether (3 × 20 ml). The ethereal solution was washed with distilled water (3 × 20 ml), dried over anhydrous magnesium sulfate and concentrated under reduced pressure. The residue was purified by preparative TLC on silica gel (light petroleum-ethyl acetate = 19:1) to afford the (*E*)-butyl cinnamate (0.161 g, 79%).

(*E*)-*Butyl cinnamate*[16]: ν_{max}(film)/cm^{-1} 3060, 2925, 2870, 1710, 1630, 1170, 825; δ_H ($CDCl_3$) 0.96 (3H, t, J7.5 Hz), 1.17–1.98 (4H, m), 4.20 (2H, t, *J*6.0Hz), 6.40 (1H, d, *J*15.0Hz), 7.04–7.80 (6H, m).

(*E*)-*Butyl 4-chlorocinnamate*[16]: ν_{max}(film)/cm^{-1} 3060, 2930, 2865, 1710, 1635, 1165, 850; δ_H ($CDCl_3$) 0.96 (3H, t, *J*7.5 Hz), 1.15–1.98 (4H, m), 4.20 (2H, t, *J*6.0 Hz), 6.36(1H, d, J15.0 Hz), 7.12–7.64 (5H, m).

(*E*)-*Butyl 4-methoxycinnamate*[16]: ν_{max}(film)/cm^{-1} 3050, 2930, 2860, 1710, 1635, 1170,1254, 985, 830; δ_H ($CDCl_3$) 0.96 (3H, t, *J*7.5 Hz), 1.15–1.95 (4H, m), 3.84 (3H, s), 4.20 (2H, t, *J*6.0 Hz), 6.36 (1H, d, *J*15.0 Hz), 6.84(2H, d, *J*9.0 Hz), 7.42 (2H, d, *J*9.0 Hz), 7.65 (1H, d, *J*15.0 *Hz*).

(*E*)-*Butyl 3-nitrocinnamate*: m.p. 56–57°C (Found: C, 62. 86; H, 6.25; N, 5.38. $C_{13}H_{15}NO_4$ requires C, 62. 65; H, 6.02; N, 5.62%); ν_{max} (KBr)/cm^{-1} 3070, 2920, 2860, 1710, 1640, 1520, 1356, 970; δ_H ($CDCl_3$) 0.96 (3H, t, *J*7.5 Hz), 1.18–1.98 (4H, m), 4.22 (2H, t, *J*6.0 Hz), 6.60(1H, d, *J*15.0 Hz), 7.47–8.39 (5H, m).

(*E*)-*Butyl 4-nitrocinnamate*: MP 68–69°C (lit[16]. 68–70°C); ν_{max} (KBr)/cm^{-1} 3070, 2920, 2860, 1710, 1640, 1515, 1340, 840; δ_H

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 1 Palladium-catalysed arylation of butyl acrylate and acrylamide with aryl iodides in water[a]

Entry	ArI	Y	Conditions	Product yield/%[b]
1	C_6H_5I	CO_2Bu	90°C, 6h	(*E*)-$C_6H_5CH{=}CHCO_2Bu$(79)
2	4-ClC_6H_4I	CO_2Bu	90°C, 4h	(*E*)-4-$ClC_6H_4CH{=}CHCO_2Bu$(84)
3	4-$CH_3OC_6H_4I$	CO_2Bu	90°C, 8h	(*E*)-4-$CH_3OC_6H_4CH{=}CHCO_2Bu$(72)
4	3-$O_2NC_6H_4I$	CO_2Bu	90°C, 6h	(*E*)-3-$O_2NC_6H_4CH{=}CHCO_2Bu$(81)
5	4-$O_2NC_6H_4I$	CO_2Bu	90°C, 4h	(*E*)-4-$O_2NC_6H_4CH{=}CHCO_2Bu$(87)
6	4-$CH_3C_6H_4I$	CO_2Bu	90°C, 8h	(*E*)-4-$CH_3C_6H_4CH{=}CHCO_2Bu$(63)
7	C_6H_5I	$CONH_2$	100°C, 7h	(*E*)-$C_6H_5CH{=}CHCONH_2$(68)
8	4-ClC_6H_4I	$CONH_2$	100°C, 5h	(*E*)-4-$ClC_6H_4CH{=}CHCONH_2$(83)
9	4-$CH_3OC_6H_4I$	$CONH_2$	100°C, 10h	(*E*)-4-$CH_3OC_6H_4CH{=}CHCONH_2$(70)
10	4-$HO_2CC_6H_4I$[c]	$CONH_2$	100°C, 8h	(*E*)-4-$HO_2CC_6H_4CH{=}CHCONH_2$(73)
11	3-$HO_2CC_6H_4I$[c]	$CONH_2$	100°C, 8h	(*E*)-3-$HO_2CC_6H_4CH{=}CHCONH_2$(79)
12	3-$O_2NC_6H_4I$	$CONH_2$	100°C, 6h	(*E*)-3-$O_2NC_6H_4CH{=}CHCONH_2$(81)
13	4- $O_2NC_6H_4I$	$CONH_2$	100°C, 5h	(*E*)-4-$O_2NC_6H_4CH{=}CHCONH_2$(85)
14	4-$CH_3C_6H_4I$	$CONH_2$	100°C, 8h	(*E*)-4-$CH_3C_6H_4CH{=}CHCONH_2$(65)

[a] Arylation of butyl acrylate and acrylamide with aryl iodide were carried out with 1 mmol of aryl iodide, 2 mmol of butyl acrylate or acrylamide, 1.5 mmol of K_2CO_3, 0.1 mmol of Bu_4NBr and 0.02 mmol of palladium acetate in 2.5 ml of water. [b] Yields are of isolated, pure products and based on the aryl iodides. [c] K_2CO_3 (2 mmol) was used.

($CDCl_3$) 0.96 (3H, t, *J*7.5 Hz), 1.18–2.05 (4H, m), 4.24 (2H, t, *J*6.0Hz), 6.58 (1H, d, *J*15.0 Hz), 7.56–7.91 (3H, m), 8.10–8.42 (2H, m).

(*E*)-*Butyl 4-methylcinnamate*[16]: ν_{max} (film)/cm^{-1} 3030, 2930, 2860, 1715, 1640, 1175, 830; δ_H ($CDCl_3$) 0.96 (3H, t, *J*7.5 Hz), 1.14–1.95 (4H, m), 2.34 (3H, s), 4.22 (2H, t, *J*6.0 Hz), 6.36 (1H, d, *J* 15.0 Hz), 7.05–7.78 (5H, m).

Typical procedure for the synthesis of (*E*)-cinnamamides

A mixture of acrylamide (2 mmol), iodobenzene (1 mmol), $Pd(OAc)_2$ (0.02 mmol), Bu_4NBr (0.1 mmol) and K_2CO_3 (1.5 mmol) in H_2O (2.5 ml) was stirred vigorously under nitrogen at 100°C for 7 h. The reaction mixture was cooled and filtered, the solid crude product was washed with water (3 × 10 ml), extracted with ethanol (2 × 20 ml). The extracts was concentrated under reduced pressure and recrystallised from ethanol to give the (*E*)-cinnamamide (0.101 g, 68%).

(*E*)-*Cinnamamide*: M.p. 143–144°C (lit[17]. 144°C); ν_{max} (KBr)/cm^{-1} 3370, 3165, 1665, 1600, 969, 760, 700; δ_H (DMSO-d_6) 6.70 (1H, d, *J*16.0 Hz), 7.33–7.69 (6H, m).

(*E*)-*4-Chlorocinnamamide*: M.p. 210–211°C (lit[17]. 212°C); ν_{max} (KBr)/cm^{-1} 3335, 3150, 1670, 1090, 990, 830; δ_H (DMSO-d_6) 6.65 (1H, d, *J*16.0 Hz), 7.36–7.69 (5H, m).

(*E*)-*4-Methoxycinnamamide*: M.p. 195–196°C (lit[17]. 195°C); ν_{max} (KBr)/cm^{-1} 3345, 3185, 1665, 1254, 1170, 985, 830; δ_H (DMSO-d_6) 3.86 (3H, s), 6.53 (1H, d, *J*16.0 Hz), 6.96 (2H, d, *J*9.0 Hz), 7.45 (2H, d, *J*9.0 Hz), 7.74 (1H, d, *J*16.0 Hz).

(*E*)-*4-Carboxycinnamamide*: M.p. 305–306°C (lit[17]. 308°C); ν_{max} (KBr)/cm^{-1} 3355, 3160, 2525–3159 (br), 1685, 1637, 977, 962, 840; δ_H (DMSO-d_6) 6.73 (1H, d, *J*16.0 Hz), 7.43–8.05 (5H, m).

(*E*)-*3-Carboxycinnamamide*: M.p. 262–263°C (Found: C, 63.08; H, 4.85; N, 7.12. $C_{10}H_9NO_3$ requires C, 62.83; H, 4.71; N, 7.33%); ν_{max} (KBr)/cm^{-1} 3360, 3165, 2530–3162 (br), 1680, 1640, 970; δ_H (DMSO-d_6) 6.75 (1H, d, *J*16.0 Hz), 7.45–8.10 (5H, m).

(*E*)-*3-Nitrocinnamamide*: M.p. 194–195°C (lit[18]. 195–196°C); ν_{max} (KBr)/cm^{-1} 3452, 3155, 1670, 1520, 1356, 970; δ_H (DMSO-d_6) 6.80 (1H, d, *J*16.0Hz), 7.45–8.35(5H, m).

(*E*)-*4-Nitrocinnamamide*: M.p. 215–216°C (lit[17]. 216°C); ν_{max} (KBr)/cm^{-1} 3379, 3178, 1668, 1520, 1344, 980; δ_H (DMSO-d_6) 6.87 (1H, d, *J*16.0 Hz), 7.50–8.31 (5H, m).

(*E*)-*4-Methylcinnamamide*: M.p. 187–189°C (lit[18]. 189–190°C); ν_{max} (KBr)/cm^{-1} 3325, 3150, 1668, 1391, 990, 815; δ_H(DMSO-d_6) 2.32 (3H, s), 6.60 (1H, d, *J*16.0Hz), 7.15–7.56 (5H, m).

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