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Arylation of Acrylamide and Acrylonitrile with Arenediazonium Salts Catalyzed by Palladium Acetate

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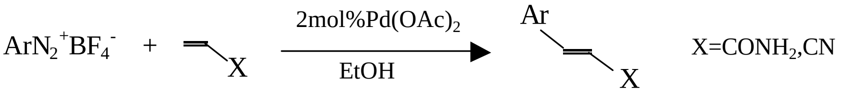
Abstract: Arylation of acrylamide and acrylonitrile were carried out with various arenediazonium tetrafluoroborates in the presence of a catalytic amount of $Pd(OAc)_2$ in ethanol and a variety of substituted (E)–cinnamamides and (E)–cinnamonitriles were obtained in high yields under mild reaction conditions.

Keywords: Arylation, arenediazonium salt, cinnamamide, cinnamonitrile.

In recent years, palladium catalyzed arylation of olefins, the Heck reaction, has evolved as a powerful synthetic tool for organic chemists[1]. Since its discovery in the early seventies[2], the reaction has undergone several modifications especially with regard to solvents, catalysts and additives. As a result, today Heck reaction is the most widely used transition metal catalyzed carbon-carbon bond forming reaction in organic synthesis[3]. However, despite all these modifications, little attention has so far been given to the choice of the aromatic component in Heck reactions which, to date, remains largely confined to the conventional aryl halides (I, Br) and triflates. Kikukawa and coworkers[4-6] reported that arylation of olefins also could be realized by using arenediazonium salts as arylating agents in the presence of bis (dibenzylideneacetone) palladium(0) [$Pd(dba)_2$] as the catalyst. Recently, Heck reaction of arenediazonium salts with olefins such as styrene, acrylic acid esters has been reported to be conveniently carried out in the presence of $Pd(OAc)_2$ in ethanol[7-9]. However, to our knowledge, there is no specific paper regarding Heck arylation of acrylamide and acrylonitrile with arenediazonium salts. In this paper, we wish to report Heck arylation of acrylamide and acrylonitrile with various arenediazonium tetrafluoroborates in the presence of a catalytic amount of $Pd(OAc)_2$ in ethanol, which is shown in **Scheme 1.**

Scheme 1



Treatment of phenyldiazonium (2 mmol) with acrylamide (2.5 mmol) in ethanol (20 mL) at 80°C for 4 h in the presence of a catalytic amount of $Pd(OAc)_2$ (2 mol%) afforded (E)–cinnamamide in 78% yield. When acetonitrile, chloroform, or DMF was used as the solvent, no significant reaction was observed. We applied the reaction to various arenediazonium salts in ethanol. The typical results are summarized in **Table 1**. As is evident, arylation of acrylamide with various arenediazonium salts proceeded smoothly and a variety of substituted (E)–cinnamamides were obtained in high yields. A very wide range of substituents may be present in the benzene ring of the arenediazonium salt and the nature of the substituents does not exert significant effect on the yields of the reactions.

The arylation reaction of acrylonitrile with various arenediazonium tetrafluoro-borates also readily took place in the presence of $Pd(OAc)_2$ in ethanol, and (E)–cinnamonitriles were obtained in high yields. The results are also listed in **Table 1.** As seen from **Table 1,** this reactin is also suitable for a variety of functional groups, both strongly electron donating and withdrawing substituents can be present. All (E)–cinnamamides and (E)–cinnamonitriles gave satisfactory mp, IR and ^1H NMR spectra.

Table 1 Arylation of acrylamide and acrylonitrile with arenediazonium tetrafluoroborates[a]

Entry	Ar	X	mp/℃(lit)	Product	Isolated yield(%)[b]
1	C_6H_5	$CONH_2$	144-145(144)[10]	(E)-$C_6H_5CH{=}CHCONH_2$	78
2	4-$CH_3C_6H_4$	$CONH_2$	191(189-190)[11]	(E)-4-$CH_3C_6H_4CH{=}CHCONH_2$	82
3	4-$CH_3OC_6H_4$	$CONH_2$	195-196(195)[10]	(E)-4-$CH_3OC_6H_4CH{=}CHCONH_2$	85
4	4-ClC_6H_4	$CONH_2$	210-211(212)[10]	(E)-4-$ClC_6H_4CH{=}CHCONH_2$	86
5	4-BrC_6H_4	$CONH_2$	214(215-216.5)[12]	(E)-4-$BrC_6H_4CH{=}CHCONH_2$	89
6	4-$O_2NC_6H_4$	$CONH_2$	216(217)[11]	(E)-4-$O_2NC_6H_4CH{=}CHCONH_2$	87
7	3-$O_2NC_6H_4$	$CONH_2$	197(195-196)[11]	(E)-3-$O_2NC_6H_4CH{=}CHCONH_2$	84
8	C_6H_5	CN	19-20(22.5)[13]	(E)-$C_6H_5CH{=}CHCN$	81
9	4-$CH_3C_6H_4$	CN	69-70(70-71)[14]	(E)-4-$CH_3C_6H_4CH{=}CHCN$	84
10	3-$CH_3C_6H_4$	CN	Oil[14]	(E)-3-$CH_3C_6H_4CH{=}CHCN$	80
11	4-ClC_6H_4	CN	82-83(84-85)[14]	(E)-4-$ClC_6H_4CH{=}CHCN$	85
12	4-$CH_3OC_6H_4$	CN	62-63(64)[14]	(E)-4-$CH_3OC_6H_4CH{=}CHCN$	83
13	4-BrC_6H_4	CN	101-102(102-104)[14]	(E)-4-$BrC_6H_4CH{=}CHCN$	86

a) Carried out with 1 mmol of arenediazonium tetrafluoroborate, 1.5 mmol of acrylamide or acrylonitrile and 0.02 mmol of $Pd(OAc)_2$ in EtOH(10 mL) at 80°C.

b) Isolated yield was based on the arenediazonium tetrafluoroborate.

Synthesis of (E)–cinnamamides and (E)–cinnamonitriles are very significant because of their uses as important organic intermediates. Arylation of acrylamide and acrylonitrile with aryl halides by Heck's method needs aryl bromides or iodides. These reagents are often not so available. The present method for preparing (E)–cinnamamides and (E)–cinnamonitriles has advantages of readily available starting materials (arenediazonium tetrafluoroborates), short reaction times, good yields under mild conditions and operational simplicity.

Experimental

Arenediazonium tetrafluoroborates were prepared by the literature procedure[15]. Melting points were taken with a Yanoco micro melting pointing apparatus and the thermometer is uncorrected. IR spectra were obtained using a Shimadzu IR-435 grating spectrophotometer. ^{1}H NMR spectra were recorded on a JEOL FX-90Q (90MHz) instrument with Me_4Si as an internal standard with $CDCl_3$ or DMSO-D_6 as the solvent. Acrylonitrile was distilled prior to use. Other reagents were of commercial quality from freshly opened containers and were used without further purification.

General procedure for the arylation of acrylamide

A mixture of arenediazonium tetrafluoroborate (1 mmol), acrylamide (1.5 mmol) and $Pd(OAc)_2$ (0.02 mmol) in EtOH (10 mL) was stirred under nitrogen at 80°C for 4 h. The mixture was cooled and filtered. The filtrate was concentrated under reduced pressure and the resulting solid product was washed with water (3×10 mL). The crude product was purified by recrystallizing from EtOH.

General procedure for the arylation of acrylonitrile

A mixture of arenediazonium tetrafluoroborate (1 mmol), acrylonitrile (1.5 mmol) and $Pd(OAc)_2$ (0.02 mmol) in EtOH (10 mL) was stirred under nitrogen at 80°C for 4 h. The mixture was cooled and filtered. The filtrate was concentrated under reduced pressure and the resulting crude product was dissolved in ether (50 mL). The ethereal solution was washed with water (3×10 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by preparative TLC on silica gel (petroleum:ethyl acetate=5:1).

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