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PALLADIUM-CATALYZED DESULFONYLATIVE COUPLING OF ARYLSULFONYL CHLORIDES WITH ACRYLATE ESTERS UNDER SOLID-LIQUID PHASE TRANSFER CONDITIONS

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Summary: *The reaction of arylsulfonyl chlorides with acrylate esters in the presence of a catalytic amount of* $PdCl_2(PhCN)_2$ *under solid-liquid phase transfer conditions gives the corresponding 3-aryl-2-propenoates in good yields.*

The palladium-catalyzed coupling reaction of aryl bromides or iodides with alkenes is a useful method for preparation of styrene derivatives.[1] While aryl chlorides can be hardly reacted, aryldiazonium salts and the related compounds,[2] aroyl chlorides,[3] aryl triflates,[4] and arylazo aryl sulfones[5] have been successfully used in place of aryl halides. We have reported that, in the presence of a catalytic amount of a palladium complex, arylsulfonyl chlorides react with carbon monoxide and titanium(IV) alkoxides accompanied by desulfonylation to give aromatic esters in reasonable yields.[6] It was expected that the palladium-catalyzed arylation of alkenes could be achieved by use of the sulfonyl chlorides, readily available from the corresponding sulfonic acids. The arylation using the sulfonyl chlorides in the presence of N-ethylmorpholine as base has been indeed disclosed in a recent publication by Kasahara et al.[7] However, the product yields were unfortunately moderate to low. We now report our findings that the reaction of arylsulfonyl chlorides **1** with acrylate esters **2** in the presence of a catalytic amount of dichlorobis(benzonitrile)palladium $PdCl_2(PhCN)_2$ under solid-liquid phase transfer conditions[8] efficiently proceeds to give the corresponding 3-aryl-2-propenoates **3** in good to excellent yields (Table).[9,10]

$$\underset{\mathbf{1}}{\mathrm{ArSO_2Cl}} \quad + \quad \underset{\mathbf{2}}{\mathrm{CH_2{=}CHCOOR}} \xrightarrow[\mathrm{K_2CO_3/BzOct_3NCl}]{\mathrm{PdCl_2(PhCN)_2}} \underset{\mathbf{3}}{\mathrm{ArCH{=}CHCOOR}}$$

The following example is representative. A mixture of 1-naphthalenesulfonyl chloride (2 mmol), n-butyl acrylate (5 mmol), potassium carbonate (3 mmol), $PdCl_2(PhCN)_2$ (0.05 mmol), and benzyltrioctylammonium chloride $BzOct_3NCl$ (0.3 mmol) in m-xylene (4 cm^3) was heated at 140 ^oC for 4 h with stirring under nitrogen. Formation of butyl 3-(1-naphthyl)-2-propenoate (95 %) was confirmed by GC-MS analysis. The ester was also isolated in 90 % yield by column chromatography on silica gel using benzene-hexane as eluant.

Table. Palladium-catalyzed desulfonylative coupling of aryl sulfonyl chlorides with acrylate esters^{a}

Ar in **1**	R in **2**	Base	PTC	Yield of **3** (%)^{b,c}
1-naphthyl	n-Bu	K_2CO_3	$BzOct_3NCl$	95
1-naphthyl	n-Bu	K_2CO_3	$MeOct_3NCl$	91
1-naphthyl	n-Bu	K_2CO_3	Bu_4NCl	36
1-naphthyl	n-Bu	K_2CO_3	Et_4NCl	8
1-naphthyl^{d}	n-Bu	K_2CO_3	$BzOct_3NCl$	75
1-naphthyl	n-Bu	Oct_3N		45
1-naphthyl	Et	K_2CO_3	$BzOct_3NCl$	94
1-naphthyl	Et	Bu_3N		38
2-naphthyl	n-Bu	K_2CO_3	$BzOct_3NCl$	84
6-methyl-2-naphthyl	n-Bu	K_2CO_3	$BzOct_3NCl$	89
phenyl	n-Bu	K_2CO_3	$BzOct_3NCl$	63
4-methylphenyl	n-Bu	K_2CO_3	$BzOct_3NCl$	72
4-chlorophenyl	n-Bu	K_2CO_3	$BzOct_3NCl$	90

^{a}The reaction was carried out in m-xylene at 130-140 °C for 4 h under nitrogen. [**1**]:[**2**]:[Base]:[PTC]:[$PdCl_2(PhCN)_2$]=2:5:3:0.3:0.05. ^{b}Yield based on **1** charged was determined by GLC analysis. ^{c}Each product had exclusively (E)-configuration. ^{d}[$Pd(OAc)_2$]=0.05.

While the present reaction was catalyzed by a number of palladium species, $Pd(OAc)_2$, $PdCl_2$, $PdCl_2(PhCN)_2$, $PdCl_2(PPh_3)_2$, $Pd(PPh_3)_4$, and Pd-black, among these species, $PdCl_2(PhCN)_2$ gave the most satisfactory result. The efficiency of the quarternary ammonium chlorides tested as the phase transfer catalysts (PTC) decreased as follows $BzOct_3NCl \geq MeOct_3NCl >> Bu_4NCl >> Et_4NCl$, indicating that the use of a PTC having high lipophilicity is essential for a high yield coupling.

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