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Palladium-Catalyzed Desulfonylative Homo-Coupling of Arylsulfonyl Chlorides in the Presence of Titanium(IV) Isopropoxide

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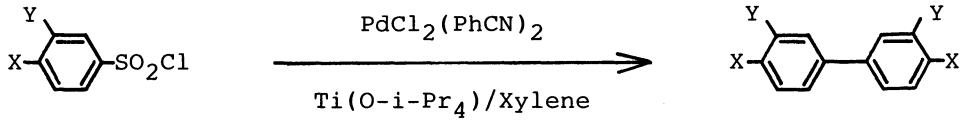
The desulfonylative homo-coupling of arylsulfonyl chlorides efficiently proceeds on treatment with titanium(IV) isopropoxide in the presence of a catalytic amount of $PdCl_2(PhCN)_2$ to give the corresponding biaryls in good yields.

The palladium-catalyzed coupling reaction of aryl halides with unsaturated compounds and organometallic reagents is a useful tool for preparation of substituted aromatic compounds and there have been extensive studies of the reaction.$^{1)}$ On the other hand, catalytic homo-coupling reaction of the halides also occurs in the presence of an appropriate reductant to afford biaryls in reasonable yields.$^{1,2)}$

In the course of our study of carbonylation$^{3)}$ and vinylation$^{4)}$ reactions using arylsulfonyl chlorides in place of aryl halides, we found that homo-coupling reaction of the sulfonyl chlorides (1) efficiently proceeds accompanied by desulfonylation on treatment with titanium(IV) isopropoxide $Ti(O\text{-}i\text{-}Pr)_4$ in the presence of a catalytic amount of dichlorobis(benzonitrile)palladium $PdCl_2(PhCN)_2$ to give biaryls (2).$^{5)}$



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a; X=Cl, Y=H: b; X=F, Y=H: c; X=Br, Y=H: d; X=H, Y=Cl:
e; X=Y=H: f; X=Me, Y=H: g; X=Y=Cl: h; X=Cl, Y=Me

When 4-chlorobenzenesulfonyl chloride (1a) (2 mmol) was heated in the presence of $PdCl_2(PhCN)_2$ (2.5 mol%) and $Ti(O\text{-}i\text{-}Pr)_4$ (2 equiv.) in m-xylene (4 cm^3) at 140 $^{\circ}C$ for 2 h under nitrogen, 4,4'-dichlorobiphenyl (2a) was produced in a yield of 76% (Table 1). Palladium acetate also showed a good catalytic activity, but Pd-black and $PdCl_2(PPh_3)_2$ were less effective. While $Ti(O\text{-}n\text{-}Bu)_4$ could be also used in place of $Ti(O\text{-}i\text{-}Pr)_4$, the yield of 2a was considerably decreased. Other metal alkoxides $Ti(O\text{-}t\text{-}Bu)_4$, $B(O\text{-}i\text{-}Pr)_3$, and $Al(O\text{-}i\text{-}Pr)_3$ were ineffective. The biaryls (2b-h) were also isolated in fair to good yields from the reactions of 3- and/or 4-substituted benzenesulfonyl chlorides (1b-h) using $Ti(O\text{-}i\text{-}Pr)_4$ and $PdCl_2(PhCN)_2$

Table 1. Desulfonylative homo-coupling of 4-chlorobenzenesulfonyl chloride 1a[a]

Pd-catalyst	$M(OR)_n$	Yield of 2a/%[b]
$PdCl_2(PhCN)_2$	$Ti(O\text{-}i\text{-}Pr)_4$	76 (74)[c]
$Pd(OAc)_2$	$Ti(O\text{-}i\text{-}Pr)_4$	71
$PdCl_2(PPh_3)_2$	$Ti(O\text{-}i\text{-}Pr)_4$	13
Pd-black	$Ti(O\text{-}i\text{-}Pr)_4$	5
$PdCl_2(PhCN)_2$	$Ti(O\text{-}n\text{-}Bu)_4$	32
$PdCl_2(PhCN)_2$	$Ti(O\text{-}t\text{-}Bu)_4$	-[d]
$PdCl_2(PhCN)_2$	$B(O\text{-}i\text{-}Pr)_3$	-[d]
$PdCl_2(PhCN)_2$	$Al(O\text{-}i\text{-}Pr)_3$	-[d]

a) The reaction was carried out in m-xylene at 140 °C for 2 h under N_2. [1a]:[Pd]:[$M(OR)_n$]=2:0.05:4.
b) Determined by GLC analysis.
c) Isolated yield.
d) Formation of 2a was not detected.

Table 2. Desulfonylative homo-coupling of arylsulfonyl chlorides 1b-i[a]

$ArSO_2Cl$	Yield of 2/%[b]
1b	74
1c	56
1d	67
1e	51
1f	40
1g	70
1h	75
1i	66[c]

a) The reaction was carried out in m-xylene at 140 °C for 2 h under N_2. [1]:[$PdCl_2(PhCN)_2$]:[$Ti(O\text{-}i\text{-}Pr)_4$]= 2:0.05:4.
b) Isolated yield.
c) A mixture of 2i and 2i'.

(Table 2). The reaction of 1-naphthalenesulfonyl chloride (1i) gave a mixture of 1,1'- (2i) (26%) and 1,2'-binaphthyls (2i') (40%) along with naphthalene (12%).[6,7]

The present reaction as well as the carbonylation[3] and vinylation[4] using arylsulfonyl chlorides appears to be particularly advantageous, if the corresponding halide can not be obtained by direct halogenation; e.g. 1g and 1h, which are able to be prepared by chlorosulfonation of 1,2-dichlorobenzene and 2-chlorotoluene in one step.[8] In addition, the reaction can be completed in a fairly short time compared with that using aryl halides.

References

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5) Desulfonylative homo-coupling of sodium 4-toluenesulfinate using a stoichiometric amount of Na_2PdCl_4 has been reported: K. Garves, J. Org. Chem., 35, 3273 (1970); R. Selke and W. Thiele, J. Prakt. Chem., 313, 875 (1971).
6) It was confirmed that both 1i and 2i are not transformed into the corresponding β-isomers under the reaction conditions, suggesting that the isomerization occurs during the catalytic process.
7) Reaction of 1-bromonaphthalene under the same conditions used for 1 afforded naphthalene (55%), no coupling product being detected.
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