

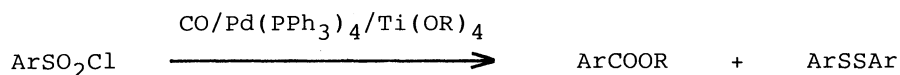
Palladium-catalyzed Desulfonylative Carbonylation of Arylsulfonyl Chlorides in the Presence of Titanium Tetraalkoxides

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The carbonylation of arylsulfonyl chlorides with a catalytic amount of tetrakis(triphenylphosphine)palladium(0) in the presence of a titanium tetraalkoxide gives the corresponding esters along with diaryl disulfides.

The palladium-catalyzed carbonylation of aryl bromides and iodides is a useful tool for the preparation of a variety of aromatic carbonyl compounds; the reaction of intermediary aroylpalladium complexes with various nucleophilic reagents gives the products.¹⁾ While aryl chlorides can be hardly carbonylated, aryldiazonium salts,²⁾ aryl triflates,³⁾ and arylborates⁴⁾ have been successfully used in place of aryl halides. We may conceive that arylsulfonyl chlorides could also be used, since Group VIII metal-catalyzed desulfonylation of them leading to aryl chlorides is considered to involve arylmetal intermediates⁵⁾ which may be transformed into the aroylmetal complexes under carbon monoxide. In spite of their ready availability, the use of the sulfonyl chlorides as the precursors of the carbonyl compounds has been seldom studied.⁶⁾

In the course of our study of the synthesis of aromatic carbonyl compounds via carbonylation,⁷⁾ we observed that the reaction of arylsulfonyl chlorides with carbon monoxide using a catalytic amount of tetrakis(triphenylphosphine)-palladium(0) Pd(PPh₃)₄ in the presence of a titanium tetraalkoxide Ti(OR)₄⁸⁾ gives the corresponding aromatic esters in good to moderate yields along with diaryl disulfides (Table 1).⁹⁾



The reaction of arylsulfonyl chlorides (2 mmol) was carried out in the presence of Pd(PPh₃)₄ (0.02-0.1 mmol) and Ti(OR)₄ (2-4 mmol) in acetonitrile at 150-160 °C under carbon monoxide (10 atm) for 4-10 h using a 40 cm³ stainless steel autoclave. The products were isolated by column chromatography on silica gel. Titanium(IV) isopropoxide was found to be more effective than titanium ethoxide and butoxide. A divalent palladium complex PdCl₂(PPh₃)₂ could be also used in place of Pd(PPh₃)₄. Although the reaction proceeded at 100 °C or under a normal pressure of carbon monoxide, the yield of the esters considerably decreased.

Table 1. Carbonylation of arylsulfonyl chlorides with Pd(PPh₃)₄ in the presence of titanium tetraalkoxides^{a)}

| Ar in ArSO ₂ Cl | R in Ti(OR) ₄ | Yield/% ^{b)} | | Ar in ArSO ₂ Cl | R in Ti(OR) ₄ | Yield/% ^{b)} | |
|-------------------------------|-----------------------------|-----------------------|--------|-------------------------------|-----------------------------|-----------------------|--------|
| | | ArCOOR | ArSSAr | | | ArCOOR | ArSSAr |
| 1-naphthyl | Et | 38 | 15 | 1-naphthyl ^{d)} | 2-Pr | 66 | 14 |
| 1-naphthyl | 2-Pr | 66 | 25 | 2-naphthyl | 2-Pr | 63 | 22 |
| 1-naphthyl ^{c)} | 2-Pr | 70 | 17 | 4-methylphenyl | 2-Pr | 53 | 40 |
| 1-naphthyl | Bu | 43 | 14 | 4-chlorophenyl | 2-Pr | 59 | 28 |

a) The reaction was carried out in acetonitrile (4 ml) at 150-160 °C under carbon monoxide (10 atm) for 4-10 h using ArSO₂Cl (2 mmol), Ti(OR)₄ (4 mmol), and Pd(PPh₃)₄ (0.1 mmol) unless otherwise noted. b) Isolated yield. c) The reaction with PdCl₂(PPh₃)₄ (0.1 mmol). d) Ti(OR)₄; 2 mmol, Pd(PPh₃)₄; 0.02 mmol.

When the reactions of 1-naphthalenesulfonyl chloride using aluminum isopropoxide (2 equiv.) and tetrabutyltin (1.5 equiv.) in place of Ti(OR)₄ were carried out in the presence of Pd(PPh₃)₄ (0.05 equiv.), isopropyl 1-naphthoate (35%) and 1-butyl naphthyl ketone (21%) were obtained, respectively.

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