CHEMISTRY LETTERS, pp. 77-78, 1989.

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

Masahiro MIURA,* Kenji ITOH, and Masakatsu NOMURA
Department of Applied Chemistry, Faculty of Engineering,
Osaka University, Suita, Osaka 565

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) $Pd(PPh_3)_4$ in the presence of a titanium tetraalkoxide $Ti(OR)_4$8) gives the corresponding aromatic esters in good to moderate yields along with diaryl disulfides (Table 1).9)

$$ArSO_2Cl \xrightarrow{CO/Pd(PPh_3)_4/Ti(OR)_4} ArCOOR \quad + \quad ArSSAr$$

The reaction of arylsulfonyl chlorides (2 mmol) was carried out in the presence of $Pd(PPh_3)_4$ (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 cm^3 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 $PdCl_2(PPh_3)_2$ could be also used in place of $Pd(PPh_3)_4$. 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 $Pd(PPh_3)_4$ in the presence of titanium tetraalkoxides[a]

Ar in	R in	Yield/%[b]		Ar in	R in	Yield/%[b]	
$ArSO_2Cl$	$Ti(OR)_4$	ArCOOR	ArSSAr	$ArSO_2Cl$	$Ti(OR)_4$	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 $ArSO_2Cl$ (2 mmol), $Ti(OR)_4$ (4 mmol), and $Pd(PPh_3)_4$ (0.1 mmol) unless otherwise noted. b) Isolated yield. c) The reaction with $PdCl_2(PPh_3)_4$ (0.1 mmol). d) $Ti(OR)_4$; 2 mmol, $Pd(PPh_3)_4$; 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 $Pd(PPh_3)_4$ (0.05 equiv.), isopropyl 1-naphthoate (35%) and 1-butyl naphthyl ketone (21%) were obtained, respectively.

References

1) J. Tsuji, "Organic Synthesis with Palladium Compound," Springer-Verlag, New York (1980); R. F. Heck, "Palladium Reagents in Organic Syntheses," Academic Press, New York (1985); M. Tanaka and T. Sakakura, Petrotech, 10, 134, 263 (1987) and references therein. 2) K. Kikukawa, K. Kono, K. Nagira, F. Wada, and T. Matsuda, J. Org. Chem., 46, 4413 (1981); K. Kikukawa, K. Kono, F. Wada, and T. Matsuda, Chem. Lett., 1982, 35; K. Kikukawa, T. Totoki, F. Wada, and T. Matsuda, J. Organomet. Chem., 270, 283 (1984). 3) S. Cacchi, P. G. Ciattini, E. Morera, and G. Ortar., Tetrahedron Lett., 27, 3931 (1986); R. E. Dolle, S. J. Schmidt, and L. I. Kruse, J. Chem. Soc., Chem. Commun., 1987, 904; Q. Y. Chen and Y. B. He., Tetrahedron Lett., 28, 2387 (1987); A. M. Echavarren and J. K. Stille, J. Am. Chem. Soc., 110, 1557 (1988). 4) T. Ohe, K. Ohe, S. Uemura, and N. Sugita, J. Organomet. Chem., 344, C5 (1988). 5) J. Blum and G. Scharf, J. Org. Chem., 35, 1895 (1970). 6) One example for the preparation of aromatic methyl esters by the carbonylation of arylsulfonyl halides with palladium acetate in the presence of triethylamine in methanol has been described in a patent literature: C. M. Lentz, J. R. Overton, and D. D. Cornell, U. S. Pat., 4507493 (1985). We could, however, obtain the esters in very poor yield by the method, the predominant products being methyl sulfonates and sulfonic acids.
7) M. Miura, F. Akase, and M. Nomura, J. Chem. Soc., Chem. Commun, 1986, 241; M. Miura, F. Akase, M. Shinohara, and M. Nomura, J. Chem. Soc., Perkin Trans. 1, 1987, 1021; M. Miura, F. Akase, and M. Nomura, J. Org. Chem., 52, 2623 (1987).
8) J. B. Woell, S. B. Fergusson, and H. Alper, J. Org. Chem., 50, 2134 (1985).
9) The following relevant works have been reported: Carbonylation of sodium 4-methylbenzenesulfinate with a stoichiometric amount of Na_2PdCl_4 in methanol gives methyl 4-methylbenzoate: K. Garves, J. Org. Chem., 35, 3273 (1970); Reaction of arylazo aryl sulfones with $Pd(PPh_3)_4$ in benzene-acetic acid under carbon monoxide affords the corresponding acids: A. Sato and N. Kamigata, 56th National Meeting of the Chemical Society of Japan, Tokyo, April 1988, Abstr., No. 1XIIA27.

(Received September 30, 1988)