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Insertion of Selenium into Zinc Carbon Bond and Application in Synthesis of Arylselenoester

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Abstract: Selenium was inserted into the zinc carbon bond of aryl zinc halides to form corresponding zinc selenoates. They reacted in THF-HMPA with acylhalides to afford the selenoesters in high yields.

Keyword: Selenium, insertion reaction, zinc carbon bond, acylhalides, selenoester.

Organoselenium compounds have attracted considerable interest as reagents and intermediates in organic synthesis. A convenient and general method to introduce a selenium group into organic molecules is through the reaction of a metal selenoate with approriate electrophiles. Recently selenoates or complexes of transition metal such as Ti[1], Zr[2], Hf[3], Sm[4], Yb[5], Cd[6] *et al.* were widely used in synthesis of organic seleno compounds. This is due to their good nucleophilicity in aprotic solvents. Their preparation can be *via* reduction cleavage of Se-Se bond, but the more convenient and simple method is *via* the insertion reaction of selenium to carbon metal bond. Zinc is a very abundant, relatively inexpensive and generally nontoxic element. Moreover organic zinc compounds can be readily prepared, but zinc selenoate has remained unexplored. In this paper we describe the preparation of zinc selenoates and their application in synthesis of selenoester .

We investigated the insertion of selenium into zinc carbon bond of aryl zinc halides to give the corresponding zinc aryl selenoates. Thus zinc selenoates reacted with acyl halid to give selenoester (**Scheme 1**).

Scheme 1

$$\mathrm{ArMgBr} \xrightarrow{\mathrm{ZnCl_2}} \mathrm{ArZnCl} \xrightarrow{\mathrm{Se}} \mathrm{ArSeZnCl} \xrightarrow{\mathrm{RCOCl}} \underset{\textbf{a-h}}{\mathrm{ArSeCOR}}$$

There are many methods for synthesis arylselenoesters[7]. However, most of them have certain disadvantages such as harsh reaction conditions, laborious, manipulation.

The present method has the advantages of easy availability of starting materials, mild reaction conditions, convenient manipulation and moderate yields.

Table 1 The mp and yield of Arylselenoesters **a-h**

Entry	Ar	R	mp °C (lit)	Yield*
a[8]	Ph	CH_3	Oil	65
b	Ph	Et	Oil	72
c	Ph	OCH_3	Oil	60
d[8]	Ph	Ph	39-40 (40)	63
e	*p*-$CH_3C_6H_4$	OCH_3	Oil	70
f[9]	*p*-$CH_3C_6H_4$	Ph	71-72 (70-71)	59
g[9]	*p*-$CH_3OC_6H_4$	Ph	98-100 (97-99)	70
h	*p*-$CH_3OC_6H_4$	CH_3	Oil	67

*isolated yields. The structure of **a-h** were confirmed by ^{1}H NMR and IR

The representative procedure for the synthesis of selenoesters as follows: to a solution of RMgBr (2.0 mmol) in 5 mL THF was added anhydrous $ZnCl_2$ (2.0 mmol) and 10 mL THF at 0°C. The mixture was stirred at r.t. for 30 minutes, then selenium (2.0 mmol) was added to the solution, which was stirred in boiling THF till the selenium disappeared. The acyl halids (2.0 mmol) and HMPA (5 mL) were added to the solution, the mixture was stirred at r.t. for 20 h.. Then the reactive mixture was diluted with 60 mL of ether. The organic phase was separated and washed with brine and dried over $MgSO_4$. The solvent was evaporated. The crude product was subjected to preparative TLC on silica gel using light petroleum-ether as eluent (30:1).

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