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INSERTION OF ELEMENTAL SELENIUM INTO ZINC CARBON BOND AND APPLICATION IN SYNTHESIS OF α -SELENOCARBONYL COMPOUND

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Abstract : Selenium inserted into the zinc carbon bond of alkyl and aryl zinc halides to form the corresponding the zinc alkyl and arylselnoates. They reacted in THF-HMPA with α -bromo carbonyl compounds to afford the α -selenocarbonyl compounds in high yields.

Recently transition metal selenoates or complexes were widely used in synthesis of organic seleno compounds¹⁻⁵. This is due to their good nucleophilicity in aprotic solvents. Zinc is a very abundant, relatively inexpensive and generally nontoxic element. But zinc selenoate has remained unexplored. In this paper we describe the preparation of zinc alkyl and arylselenoates and their application in synthesis of α -seleno carbonyl compounds.

Because organic zinc compounds can be readily prepared, we tried to develop a convenient method for the preparation of the zinc selenoates. We investigated the

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insertion of selenium into zinc carbon bond of the alkyl and aryl zinc halides. The experimental result showed that the reaction could be carried out in boiling THF and gave the corresponding zinc alkyl and aryl selenoates. The zinc selenoates reacted with α -bromocarbonyl compounds to give α -selenocarbonyl compounds in high yields (Table 1).

$$R^{1}Br \xrightarrow{Mg} R^{1}MgBr \xrightarrow{ZnCl_{2}} R^{1}ZnCl \xrightarrow{Se} R^{1}SeZnCl$$

$$\xrightarrow{BrCH_{2}COR^{2}} R^{1}SeCH_{2}COR^{2}$$

$$IhF-HMPA 60^{\circ}C R^{1}SeCH_{2}COR^{2}$$

$$Ia-h$$

 α -Seleno carbonyl compounds are very important organic intermediates⁶⁻⁹. There are several methods for their preparation. For example via the reaction of nucleophilic ArSe'Na⁺ with α -bromo carbonyl compounds, the electrophilic selenium reagent ArSeX (X : Cl, Br) with carbanions of carbonyl compounds at - 78°C¹⁰ or via the oxidation-elimination reaction of additive product of ArSeX to olefins¹¹. But some of these methods suffer from some disadvantages in terms of reaction conditions or laborious manipulation. The present method provides a new path for the synthesis of α -seleno carbonyl compounds. Moreover it has advantages of available starting materials, convenient manipulations and mild reaction conditions.

α-SELENOCARBONYL COMPOUND

Products	R ¹	R^2	Yield*
1a	Ph	OC ₂ H ₅	80
1b	p-CH ₃ C ₆ H ₄	OC_2H_5	78
1c	p-CH ₃ OC ₆ H ₄	OC_2H_5	82
1d	n-C ₄ H ₉	Ph	75
1e	C_2H_5	Ph	70
1f	n-C ₄ H ₉	p-BrC ₆ H ₄	80
1g	p-CH ₃ C ₆ H ₄	CH3	78
1 h	p-CH ₃ OC ₆ H ₄	CH ₃	78

Table 1 Synthesis of α-Selenocarbonyl Compound.

* isolated yields.

Experimental

¹HNMR spectra were recorded on PMX-60 spectrometer .IR spectra were determined on PE-683 spectrophotometer. Tetrahydrofuran was distilled from sodium benzophenone. Commercial HMPA was used.

A representative procedure for the synthesis of α -seleno carbonyl compounds as follows : To solution of RMgBr (2.0 mmol) in 5 ml THF was added at 0°C anhydrous ZnCl₂ (2.0 mmol) and 10 ml THF. 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 α -bromo carbonyl compound (2.0 mmol) and HMPA (5ml) were added to the solution, which was stirred the solution at 60°C for 20h. The reaction mixture was diluted with dilute aqueous HCl (30ml) and 60ml of ether. The organic phase was washed with saturated aqueous Na₂CO₃ solution and brine and dried with MgSO₄. The solvent was **1a** IR (cm⁻¹) 3000, 1740, 1590, 740. ¹HNMR (δ,ppm) 7.51(m,2H), 7.20(m,2H), 4.02(q,2H, J=7Hz), 3.44(s,2H), 1.13(t,3H,J=7Hz).

1b IR (cm⁻¹) 3000, 1740, 1600, 1595, 1260, 1030. ¹HNMR (δ,ppm) 7.00(d,2H,J=8Hz), 7.33(d, 2H, J=8Hz), 4.06(q,2H,J=7Hz), 3.28(s,2H), 2.28(s,3H), 1.13(t,3H,J=7Hz).

1c IR (cm⁻¹) 3000, 1740, 1600, 1580, 1595, 1170. ¹HNMR (δ,ppm)
7.40(d,2H,J=8Hz), 6.66(d, 2H,J=8Hz), 3.97(q,2H,J=7Hz), 3.66(s,3H), 3.20(s,2H),
1.13(t,3H,J=7Hz)

1d IR (cm⁻¹) 3085, 2890, 1700, 1610, 1590, 1460. ¹HNMR (δ,ppm) 0.83(t,3H,), 1.13-1.67(m,4H), 2.51(t,2H), 3.53(s,2H), 7.25-7.36(m,3H), 7.72-7.87(m,2H).

1e IR (cm⁻¹) 2980, 1680, 1610, 1590, 1460, 1280. ¹HNMR (δ,ppm) 1.31(t,3H, J=7.2Hz), 2.54(q,2H,J=7.2Hz), 3.58(s,2H), 7.28-7.40(m,3H), 7.77-7.93(m,2H).

1f IR (cm⁻¹) 3090, 2890, 1680, 1598, 1493, 1070. ¹HNMR (δ,ppm) 0.83(t,3H), 1.13-1.67(m,4H), 2.51(t,2H), 3.51(s,2H), 7.38-7.80(m,4H).

1g IR (cm⁻¹) 2940, 1710, 1600, 1495, 1236, 1020. ¹HNMR (δ,ppm) 6.90(d,2H,J=8Hz), 7.26(d,2H,J=8Hz), 3.30(s,2H), 2.23(s,3H), 2.10(s,3H).

1h IR (cm⁻¹) 2965, 1715, 1600, 1495, 820. ¹HNMR (δ,ppm) 6.66(d,2H,J=8Hz), 7.30(d,2H,J=8Hz), 3.66(s,3H), 3.28(s,2H), 2.10(s,3H).

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