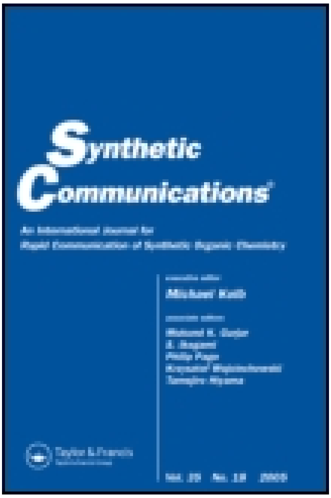

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Insertion of Elemental Selenium into Zinc Carbon Bond and Application in Synthesis of α-Selenocarbonyl Compound

Xian Huang [a] & Xin-Hua Xu [a]
[a] Department of Chemistry , Hangzhou University Hangzhou , Zhejiang, 310028, P. R. China

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

Xian Huang* and Xin-Hua Xu

Department of Chemistry, Hangzhou University
Hangzhou, Zhejiang, 310028, P. R. China

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 compounds[1~5]. 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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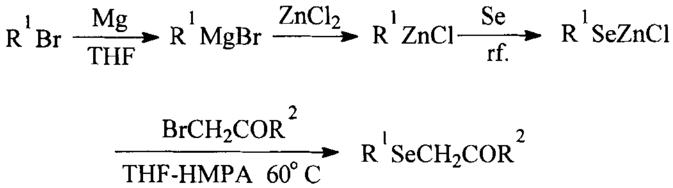
* To whom the correspondence should be addressed.

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).



$$R^1Br \xrightarrow[THF]{Mg} R^1MgBr \xrightarrow{ZnCl_2} R^1ZnCl \xrightarrow[rf.]{Se} R^1SeZnCl$$

$$\xrightarrow[THF\text{-}HMPA\ 60^\circ C]{BrCH_2COR^2} R^1SeCH_2COR^2$$

1a-h

α-Seleno carbonyl compounds are very important organic intermediates[6~9]. 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℃[10] or via the oxidation-elimination reaction of additive product of ArSeX to olefins[11]. 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.

Table 1 Synthesis of α-Selenocarbonyl Compound.

Products	R^1	R^2	Yield*
1a	Ph	OC_2H_5	80
1b	p-$CH_3C_6H_4$	OC_2H_5	78
1c	p-$CH_3OC_6H_4$	OC_2H_5	82
1d	n-C_4H_9	Ph	75
1e	C_2H_5	Ph	70
1f	n-C_4H_9	p-BrC_6H_4	80
1g	p-$CH_3C_6H_4$	CH_3	78
1h	p-$CH_3OC_6H_4$	CH_3	78

* isolated yields.

Experimental

^{1}HNMR 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℃ anhydrous $ZnCl_2$ (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℃ for 20h. The reaction mixture was diluted with dilute aqueous HCl (30ml) and 60ml of ether. The organic phase was washed with saturated aqueous Na_2CO_3 solution and brine and dried with $MgSO_4$. The solvent was evaporated. The crude product was subjected to preparative TLC on silica gel using light petroleum-ether as eluent (30:1).

1a IR (cm^{-1}) 3000, 1740, 1590, 740. ^{1}HNMR (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. ^{1}HNMR (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. ^{1}HNMR (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. ^{1}HNMR (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. ^{1}HNMR (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. ^{1}HNMR (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. ^{1}HNMR (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. ^{1}HNMR (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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