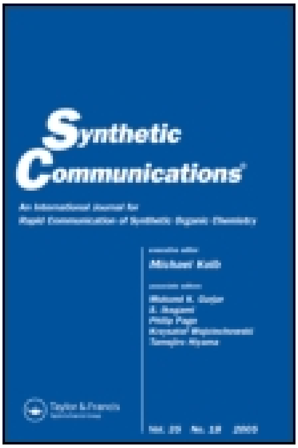

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Yunfa Zheng [b] , Weiliang Bao [a] & Yongmin Zhang [a]

[a] Department of Chemistry, Zhejiang University Xi Xi Campus, Hangzhou, 310028, China

[b] Li Shut Teacher's College, Zhejiang, 323000, China

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Synthesis of Allyl-Type Selenides and α –Selenoesters in Aqueous Media Promoted by Cadmium

Yunfa Zheng[b], Weiliang Bao[a], Yongmin Zhang[a]*
[a]*Department of Chemistry, Zhejiang University, Xi Xi Campus, Hangzhou 310028, China*
[b]*Li Shui Teacher's College, Zhejiang 323000, China*

Abstract: Promoted by metallic cadmium which was produced by reduction of $CdCl_2 \cdot H_2O$ with samarium *in situ*, allyl bromide and α –bromocarboxylates react with diorgano diselenides in aqueous solutions to give allylic-type selenides and α –selenocarboxylates in moderate to good yields.

Due to the theoretical and practical interests, much enthusiasm has been devoted to the performing of organometallic reactions in aqueous media recently since Wolinsky's pioneering work in 1977.[1] The most prominent advantage of aqueous organometallic reactions over conventional organometallic reactions is no need for strictly anhydrous organic solvents. The most commonly used metals in are indium, zinc, tin and bismuth. Very often acid catalysts, heat or sonication are required to induce the reaction promoted by zinc or tin to occur.

Although organocadmium compounds were discovered in as early as 19th century, their use as synthetic reagents was initiated much later and has been largely restricted to the preparation of ketones from acid chlorides and anhydrides.[2] Also there are some reports about metallic cadmium in organic synthesis. For example, carbonyl group in many kinds of ketones could be reduced in Cd-Mg-H_2O systems.[3] Nitro aromatics could be selectively reduced to azoxy compounds in $CdCl_2$-Zn-CH_3CN system[4]. But to the best of our knowledge there are no reports on bond-forming reaction promoted by metallic cadmium in aqueous media.

Engaged in the study of aqueous organometallic reactions, we found that metallic cadmium can promote aqueous organometallic reactions of allyl-type bromides with diorganodiselenides to give allyl selenides

$$R^1CH{=}CHCH_2Br + RSeSeR \xrightarrow[DMF/H_2O]{Cd} \underset{\textbf{1}}{R'CH{=}CHCH_2SeR}$$

α -Bromocarboxylates can also react with diselenides:

$$\underset{\displaystyle Br}{\underset{|}{R^2CHCOOR^3}} + RSeSeR \xrightarrow[DMF/H_2O]{Cd} \underset{\displaystyle SeR}{\underset{|}{R^2CHCOOR^3}}$$

2

The results are summarized in Table. The metallic cadmium we used was produced by reduction of $CdCl_2 \bullet H_2O$ with powdered samarium in DMF-H_2O or THF-H_2O solution *in situ* before allylic bromide and diorganyl diselenides were added to the reaction mixture. Also these materials could be added to DMF-H_2O or THF-H_2O solution in sequence continuously. Though the yield was not ideal when the reaction was carried out in the THF-H_2O solution (Table 1, entry 1 and 2), we got satisfactory results in DMF-H_2O solutions (Table 1, entry 3-9). Without the presence of H_2O the yield was low, probably because $CdCl_2$ was not soluble enough in DMF to be reduced to Cd. At room temperature the reaction was relatively slow. The weak acid usually needed in the Zinc promoted reactions was not necessary in the reactions here reported.

Allylic selenides have been recognized as useful synthons of allylic anion stabilized by seleno group, and they are regioselectively α -alkylated.[5] The facile

Table 1 Allylselenides

Entry	Diselenide	Bromide	Reaction Solvent*	React. Time(h)	Yield (%)
1a	$(C_6H_5Se)_2$	Allyl	THF/H_2O	4.5	67
1b	$(n\text{-}C_4H_9Se)_2$	Allyl	THF/H_2O	4.5	62
1c	$(C_6H_5Se)_2$	Allyl	DMF/H_2O	3.5	88
1d	$(n\text{-}C_4H_9Se)_2$	Allyl	DMF/H_2O	3.5	74
1e	$(n\text{-}C_6H_{13}Se)_2$	Allyl	DMF/H_2O	3.5	73
1f	$(p\text{-}CH_3C_6H_4Se)_2$	Allyl	DMF/H_2O	3.5	85
1g	$(p\text{-}ClC_6H_4Se)_2$	Allyl	DMF/H_2O	3.5	88
1h	$(C_6H_5Se)_2$	3-Bromo cyclohexene	DMF/H_2O	4.5	80
1i	$(p\text{-}ClC_6H_4Se)_2$	3-Bromo cyclohexene	DMF/H_2O	4.5	78

* *Both the ratio of DMF/H_2O and THF/H_2O are 5 to1.*

Table 2 α -Selenocarboxylates

Entry	R	R^2	R^3	React. Solvents*	React. Time(h)	Yield (%)
2a	Ph	H	C_2H_5	DMF/H_2O	3	78
2b	Ph	CH_3	C_2H_5	DMF/H_2O	3	74
2c	C_6H_{13}	H	CH_3	DMF/H_2O	4	71
2d	C_4H_9	H	CH_3	DMF/H_2O	4	68

* *The ratio of DMF/H_2O is 5 to1.*

oxidative conversion of allylic selenides to alcohols accompanied by a (2,3) sigmatropic rearrangement[6] and substitution of nucleophile for seleno groups[7] are also useful synthetic transformation. Allylic selenides could be prepared by several methods, for example, the displacement of allylic halide by selenide anions,[8] dehydroxysilylation of 2-hydroxy-3-trimethylsilyl propylselenide catalyzed by $SnCl_2$,[9] reaction of allylic acetates with diphenyl diselenide induced by samarium diiodide in the presence of a palladium catalyst.[10] We here provide a simple and easy alternative method for the synthesis of allylic selenides and α – selenocarboxylates in moderate to good yields.

EXPERIMENTAL

^{1}H NMR spectra were recorded in CCl_4 on JEOL PMX 60si spectrometer using TMS as internal standard. IR spectra were obtained on a PE 683 spectrometer. The general procedure is as follows. In a three-necked round bottomed flask fitted with a reflux condenser, and in N_2 atmosphere, were placed 2 mmol $CdCl_2 \cdot H_2O$, 2 mmol Sm powder, 10 mL DMF, 2 mL H_2O, 0.5 mmol diselenide and 1.5 mmol allylic bromide. The mixture was stirred first at the room temperature for 0.5h, then at 50° C for another 3h. The solution was cooled down to room temperature and extracted with ether (30mL × 2) after brine (10mL) and a little dilute hydrochloric acid were added. The organic layer was dried ($MgSO_4$) and solvents evaporated in vacuo. The product was separated from the residue through preparative TLC (silica gel) with petroleum ether / ether as eluent.

1a[8]: Oil, $C_9H_{10}Se$ [M^+] m/z: 197; ^{1}H NMR: 3.31(d, 2H, J=7Hz), 4.66-4.91(m, 2H), 5.46-6.15(m, 1H), 7.06-7.56(m, 5H); IR: 3095, 3080, 2940, 2870, 1645, 1590, 1485, 1445, 1075, 1065, 1022, 1000, 985, 910, 730, 685cm^{-1}.

1b: Oil; $C_7H_{14}Se$ [M^+] m/z: 177; ^{1}H NMR: 0.87(t, 3H, J=6.0Hz), 1.23-1.90(m, 4H), 2.43(t, 2H, J=7.0Hz), 3.08(d, 2H, J=7.6Hz), 4.80-5.05(m, 2H), 5.50-6.20(m, 1H); IR: 3090, 2980, 2950, 2900, 1648, 1595, 1475, 1260, 1200, 990, 910, 740, 690 cm^{-1}.

1e: Oil; $C_9H_{18}Se$ [M^+] m/z: 205; ^{1}H NMR: 0.82(t, 3H, J=4.6Hz), 1.14-1.73(m, 8H), 2.35(t, 2H, J=6.6Hz), 3.00(d, 2H, J=6.6Hz), 4.70-4.97(m, 2H), 5.43-6.13(m, 1H); IR: 3110, 2980, 2950, 2890, 2875, 1645, 1475, 1440, 1385, 1240, 1200, 1185, 987, 908, 730, 690 cm^{-1}

1f: Oil; $C_{10}H_{12}Se$ [M^+] m/z: 211; ^1H NMR: 2.18(s, 3H), 3.32(d, 2H, *J*=7.0Hz), 4.62-4.95(m, 2H), 5.38-6.13(m, 1H), 6.80-7.35(m, 4H); IR: 3085, 3040, 2940, 2880, 1645, 1495, 1435, 1305, 1015, 985, 795 cm^{-1}

1g[11]: Oil; C_9H_9ClSe [M^+] m/z: 231; ^1H NMR: 3.35(2H, d, *J*=7.2Hz), 4.67-4.93(m, 2H), 5.47-6.17(m, 1H), 7.04-7.49(m, 4H), IR: 3080, 3070, 2960, 2890, 1645, 1570, 1480, 1395, 1090, 1010, 815, 725 cm^{-1}.

1h[10]: Oil; $C_{12}H_{14}Se$ [M^+] m/z: 237; ^1H NMR: 1.59-1.93(m, 6H), 3.82(m, 1H), 5.30-5.91(m, 2H); 3090, 3080, 3045, 2950, 2880, 1590, 1485, 1445, 1260, 1180, 1075, 1065, 1020, 1000, 865, 735, 685 cm^{-1}.

1I: Oil; $C_{12}H_{13}ClSe$ [M^+] m/z: 271; ^1H NMR: 1.53-2.06(m, 6H), 3.75(m, 1H), 5.47-5.83(m, 2H), 7.00-7.43(m, 4H); IR: 3100, 3050, 2950, 1655, 1480, 1395, 1300, 1260, 1180, 1090, 1012, 985, 920, 865, 810, 725 cm^{-1}.

2a: Oil; $C_{10}H_{12}O_2Se$ [M^+] m/z: 243; ^1H NMR: 1.20(t, 3H, *J*=7.0Hz), 3.30(s, 2H), 4.04(q, 2H, *J*=7Hz), 7.06-7.23(m, 3H), 7.37-7.60(m, 2H); IR: 3090, 3010, 2960, 1750, 1590, 1485, 1450, 1270, 1110, 1025, 740, 690 cm^{-1}.

2b: Oil; $C_{11}H_{14}O_2Se$ [M^+] m/z: 257; ^1H NMR: 1.20(t, 3H, *J*=7.0Hz), 1.72(d, 3H, *J*=6.8Hz), 3.92-4.38(m, 3H), 7.05-7.23(m, 3H), 7.37-7.61(m, 2H); IR: 3090, 3010, 2955, 1745, 1590, 1480, 1450, 1275, 1110, 1025, 1000, 735, 690 cm^{-1}.

2c: Oil; $C_9H_{18}O_2Se$ [M^+] m/z: 237; ^1H NMR: 0.83(t, 3H, *J*=4Hz), 1.20-1.70(m, 8H), 2.63(t, 2H, *J*=6.8Hz), 2.93(s, 2H), 3.58(s, 3H); IR: 2980, 2950, 2880, 1755, 1445, 1275, 1120, 1020cm^{-1}

2d: Oil; $C_7H_{14}O_2Se$ [M^+] m/z: 209; ^1H NMR: 0.88(t, 3H, *J*=6.0Hz), 1.20-1.81(m, 4H), 2.65(t, 2H, *J*=7.0Hz), 2.93(s, 2H), 3.57(s, 3H); IR: 2990, 2950, 2900, 1758, 1748, 1445, 1570, 1120, 1020 cm^{-1}.

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