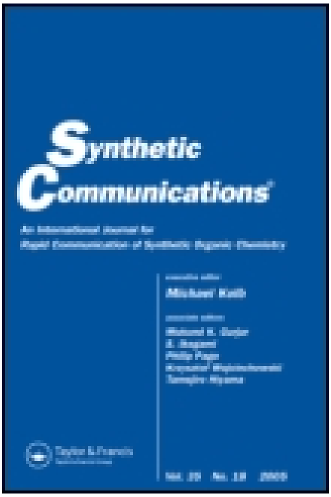

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A Novel Synthesis of Allyl and Propargyl Selenides Promoted by Indium

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A NOVEL SYNTHESIS OF ALLYL AND PROPARGYL SELENIDES PROMOTED BY INDIUM

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Abstract: Promoted by indium, allylic and propargyl bromides react with diorganyl diselenides in THF to give allylic and propargyl selenides in moderate to good yields.

The application of indium in organic synthesis is receiving growing attention. For example, the uses of indium metal in Reformatsky reaction[1] and in Barbier type reaction with carbonyl compounds[2] and with imines[3] have been documented. The addition of allyl indium reagents to carbon-carbon triple bond[4] and carbonyl compounds[5] are reported. Also more recently the coupling of imines promoted by indium metal is known.[6] However few reaction promoted by indium concerns the synthesis of selenium and tellurium containing compounds.

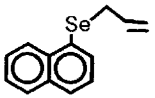
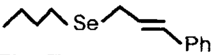
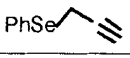
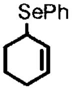
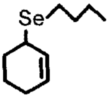
Allylic selenides are important synthetic intermediates, for selenium could stabilize α -carbanions of the allylic systems while α -carbon is deprotonated.[7]

Rearrangement of allylic selenides,[8] cleavage of C-Se bond and substitution of seleno group by alkyl or other functioal group,[9] are also useful in organic synthesis. We report herein a novel synthesis of allyl and propargyl selenides via reactions of allyl and propargyl bromides with diselenides promoted by indium:

$$R'CH{=}CHCH_2Br + RSeSeR \xrightarrow[\text{rt, or }\Delta]{\text{In/ THF}} R'CH{=}CHCH_2SeR$$

$$CH{\equiv}C{-}CH_2Br + RSeSeR \xrightarrow[\Delta]{\text{In / THF}} CH{\equiv}C{-}CH_2SeR$$

TABLE Reaction Conditions and Yields

Entry	Product	Temp.(℃)	Time(h)	Yield(%)
1	$PhSeCH_2CH{=}CH_2$	rt	12	80
2	$p\text{-}ClC_6H_4SeCH_2CH{=}CH_2$	60	24	76
3	$CH_3(CH_2)_5SeCH_2CH{=}CH_2$	60	24	71
4		70	24	55
5		rt	12	64
6		60	24	62
7		60	24	56
8		rt	8	91
9		rt	8	89

Allylic selenides could be prepared by several methods, for example, the displacement of allylic halide by selenide anions,[10] dehydroxysilylation of 2-hydroxy-3-trimethylsilylpropylselenide catalyzed by $SnCl_2$,[11] reaction of allylic acetates with diphenyl diselenide induced by samarium diiodide in the presence of a palladium catalyst.[12] Some of the methods suffer from disadvantages, for example, strong base (EtONa) and heavy poisonous starting material (PhSeH) were used[10]. We here provide a simple and easy alternative method for the synthesis of allylic and propargyl selenides in moderate to good yields.

EXPERIMENTAL

^1H 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 (neat). The reaction were performed in a Schlenk type glass apparatus and under a nitrogen atmosphere.

General procedure: In a 50mL three-necked round bottomed flask are placed 1.5 mmol indium in the form of small grains cut from a bar of indium metal, 1.5 mmol diorganyl diselenide, 3 mmol allylic bromide and 20 mL THF. The mixture is stirred under nitrogen at specified temperature for a given time, until the indium grains are almost consumed. The mixture is extracted with ether twice (30mL × 2) after brine (10mL) is added. Organic phase is worked as usual and the solvents are evaporated in vacuum. The product is separated from residue through preparative TLC (silica gel) with petroleum ether or petroleum ether/ether as eluent.

1[10]: Oil, ^1H 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, 685.

2[13]: Oil, ^{1}H 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.

3: Oil, ^{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.

4: Oil, ^{1}H NMR: 3.36(d, 2H, J=7.8Hz), 4.55-4.81(m, 2H), 5.47-6.18(m, 1H), 7.22-7.76(m, 7H), IR: 3075, 2950, 1646, 1605, 1510, 1440, 1398, 1276, 1255, 1130, 1010, 960, 915, 780, 768, 650, 615.

5[12]: Oil, ^{1}H NMR: 3.95-4.15(m, 2H), 5.84-6.59(m, 2H, while 3.95-4.15 peaks are irradiated they become AB system with J=15.6Hz), 7.12-7.43(10H, m); IR: 3110, 3085, 2940, 2870, 1690, 1640, 1505, 1460, 1370, 1240, 1125, 1030, 970, 920, 745, 690.

6: Oil, ^{1}H NMR: 0.84(t, 3H, J=4.6Hz), 1.15-1.76(m, 4H), 2.40(t, 2H, J=6.8Hz), 3.93-4.17(m, 2H), 5.84-6.60(m, 2H), 7.03-7.50(m, 5H); IR: 3100, 3080, 3050, 2980, 2950, 2890, 2880, 1690, 1640, 1610, 1505, 1460, 1260, 1210, 1125, 1070, 1030, 970, 740, 690.

7[14]: Oil, ^{1}H NMR: 1.98(t, 1H, J=2.6Hz), 3.28(d, 2H, J=2.6Hz), 7.03-7.52(m, 5H); IR: 3320, 3090, 3080, 2940, 2870, 1700, 1590, 1485, 1445, 1305, 1280, 1070, 1025, 1000, 860, 735, 685.

8[12]: Oil, ^{1}H 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.

9: Oil, ^{1}H NMR: 0.83(t, 3H, J=5.4Hz), 1.12-2.13(m, 13H), 2.43(t, 2H, J=6.4Hz), 3.43(m, 1H), 5.30-5.83(m, 2H); 3045, 2980, 2950, 2880, 2860, 1455, 1385, 1260, 1250, 1180, 1080, 1035, 1000, 985, 865, 730.

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