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A Novel Synthesis of Allyl and Propargyl Selenides In Aqueous Media Promoted by Indium

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Abstract: Allylic and propargyl bromides react smoothly with diorganyl diselenides in aqueous media to give allylic and propargyl selenides in moderate to good yields. The reaction need not be carried out in inert atmosphere. The speed is quicker than the same reactions in organic media.

There has been considerable interest in performing organometallic reactions in aqueous media recently.[1,2] The most commonly used metals in aqueous organometallic reactions are zinc, tin and indium.[1,2] Very often, acid catalysts,[3] heat[4] or sonication[5] are required to induce the reaction promoted by zinc or tin to occur. Compared to the use of zinc and tin, the reactions with indium did not require any promoter.[6] The use of indium metal in allylation and propargylation of carbonyl compounds in aqueous media is great successful although, the type of reactions seems to have been somewhat limited.

We report herein a novel synthesis of allyl and propargyl selenides via reactions of allyl and propargyl bromides with diselenides in aqueous media promoted by indium metal:

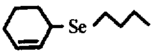
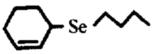
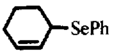
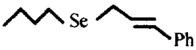
$$R'CH{=}CHCH_2Br + RSeSeR \xrightarrow[THF/H_2O]{In} R'CH{=}CHCH_2SeR$$

$$CH{\equiv}C{-}CH_2Br + RSeSeR \xrightarrow[THF/H_2O]{In} CH{\equiv}C{-}CH_2SeR$$

Allylic selenides have been recognized as useful synthons of allylic anion stabilized by seleno group, and they are regioselectively α-alkylated.[7] The facile oxidative conversion of allylic selenides to alcohols accompanied by a (2, 3) sigmatropic rearrangement[8] and substitution of nucleophile for seleno groups[9] are also useful synthetic transformation. 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] We here provide a very simple and easy alternative method for the synthesis of allylic and propargyl selenides in moderate to good yields.

As can be seen from the table, the best results are obtained using THF-H_2O as the solvent (entry 1,2 and 3) although with diphenyl diselenides as substrate, the differences in yields are not so large. Compared to the dialkyl diselenides, diphenyl diselenide is more suitable to be used as substrate(entry 4 and 6). Propargyl phenyl selenide is the main product and propadiene phenyl selenide is minor (9:1) with propargyl bromide as the substrate. The reactions were carried out in the open air and all the products were characterized by their ^1H NMR、IR and Elemental analysis.

Table Reaction Conditions and Yield

Entry	Products	Solvents(mL)	Temp.(℃)	Time(h)	Yield(%)
1	$PhSeCH_2CH=CH_2$	$EtOH-H_2O(20/1)$	50	12	80
2	$PhSeCH_2CH=CH_2$	$DMF-H_2O(15/5)$	50	12	82
3	$PhSeCH_2CH=CH_2$	$THF-H_2O(15/5)$	rt.	8	85
4		$THF-H_2O(15/5)$	50	20	70
5		$EtOH-H_2O(20/1)$	50	20	46
6		$THF-H_2O(15/5)$	rt	12	75
7		$THF-H_2O(15/5)$	50	12	50
8		$THF-H_2O(15/5)$	50	20	53
9		$THF-H_2O(15/5)$	40	20	60
10	$p-ClC_6H_4SeCH_2CH=CH_2$	$THF-H_2O(15/5)$	50	20	67
11	$CH_3(CH_2)_5SeCH_2CH=CH_2$	$THF-H_2O(15/5)$	50	20	73

The general procedure is as follows. In a round bottomed flask fitted with a reflux condenser, are placed 1mmol indium in the form of small grains cut from a bar of indium metal, diorganyl diselenide (1mmol, can be seen as 2 mmol of RSe), allylic bromide(3 mmol) and solvents. The mixture is stirred at the given temperature for a given time until the indium grains are almost consumed and the solution becomes turbid. The solution is cooled to room temperature and is extracted with ether (30mL × 2) after brine (10mL) is added. Organic layer is dried ($MgSO_4$) and solvents are evaporated in vacuum. The product is seperated from residue through preparative TLC (silica gel) with petroleum ether / cyclohexane / ether as eluent.

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