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A NOVEL SYNTHESIS OF ALLYL SULFIDES IN AQUEOUS MEDIA PROMOTED BY INDIUM

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Abstract: Allyl bromides react smoothly with sodium alkyl thiosulfates promoted by indium in aqueous media to give allyl sulfides in moderate to good yields.

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 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 sulfides via reactions of allyl bromides with sodium alkyl thiosulfates in aqueous media promoted by indium metal. The results were summarized in table.

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$$CH_2=CHCH_2Br + RSSO_3Na \xrightarrow[THF/H_2O]{In} CH_2=CHCH_2SR$$

Table Reaction Conditions and Yields

Entry	Products	Reaction Conditions		Yield*
		Time(h)	Temp. (℃)	(%)
1	n-$C_{16}H_{33}S-CH_2-CH=CH_2$	18	55	82
2	n-$C_{12}H_{25}S-CH_2-CH=CH_2$	18	55	83
3	n-$C_{10}H_{21}S-CH_2-CH=CH_2$	18	55	85
4	n-$C_8H_{17}S-CH_2-CH=CH_2$	18	55	80
5	n-$C_7H_{15}S-CH_2-CH=CH_2$	18	55	80
6	n-$C_6H_{13}S-CH_2-CH=CH_2$	18	55	78
7	$C_6H_5CH_2S-CH_2-CH=CH_2$	22	55	67
8	p-$ClC_6H_4CH_2S-CH_2-CH=CH_2$	22	55	70

* Yields of isolated product.

Sulfides are a class of useful synthetic intermediates, and many synthetic methods have been reported for preparation of sulfides in the last years, for example, the alkylation of thiols,[7] the reaction of alkyl halide with sodium sulfide,[8] addition of thiophol with alkene,[9] reduction of disulfides with copper in the presence of halide,[10] reduction of sulphoxides with titanium (Ⅱ) chloride,[11] deoxygenation of sulfoxides with triphenylphosphine/iodide/sodium iodide,[12] synthesis of allylthioethers via allyldialkyltelluronium salts.[13] Very recently, we have reported the reaction of organosamarium reagent with disulfides to afford allyl sulfides[14]. But the reaction must be conducted in strictly anhydrous solvents and under an inert atmosphere. We here provide a very simple and

easy alternative method for the synthesis of allyl sulfides in moderate to good yields.

Experimental Section

Tetrahydrofuran was distilled from sodium/benzophenone ketyl immediately before use, IR spectra were recorded on a PE-683 spectrometer, ^1H NMR spectra were obtained with a PMX-60 spectrometer in CCl_4 solution using TMS as internal standard.

The general procedure is as follows. In a round bottomed flask fitted with a reflux condenser, are placed 1 mmol indium in the form of small grains cut from a bar of indium metal, 1 mmol sodium alkyl thiosulfates, 3 mmol allyl bromide, 10 ml THF and 0.5 ml water. The mixture is stirred at room temperature for 3h. Then the mixture is stirred at 55 °C for a given time (see Table) until the indium grains are almost consumed and the solution becomes turbid. The solution is cooled to room temperature and is extracted with ether (30 ml × 2) after brine (10 ml) is added. Organic layer is dried(Na_2SO_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.

1: n-$C_{16}H_{33}S-CH_2-CH=CH_2$[14], Oil, ^1H NMR: 6.02—5.37(m, 1 H), 5.17—4.75(m, 2 H), 3.09—2.37(m, 4 H), 1.75—0.83(m, 31 H), ppm; IR: 2965, 2890, 1642, 1485, 1390, 923, 728, cm^{-1}.

2: n-$C_{25}H_{35}S-CH_2-CH=CH_2$, Oil, ^1H NMR: 6.01—5.38(m, 1 H), 5.18—4.73(m, 2 H), 3.10—2.40(m, 4 H), 1.74—0.80(m, 23 H), ppm; IR: 2960,

2892,1647,1480,1390,922,725,cm^{-1}.

3:n-$C_{10}H_{21}S-CH_2-CH=CH_2$, Oil, ^1H NMR:6.01—5.40(m,1 H),5.18—4.76(m,2 H),3.11—2.39(m,4 H),1.76—0.80(m,19 H),ppm; IR:2970,2886,1645,1480,1393,920,730,cm^{-1}.

4:n-$C_8H_{17}S-CH_2-CH=CH_2$[14], Oil, ^1H NMR:5.97—5.34(m,1 H),5.14—4.70(m,2 H),3.08—2.35(m,4 H),1.72—0.78(m,15 H),ppm; IR:2964,2897,1644,1480,1395,920,725,cm^{-1}.

5:n-$C_7H_{15}S-CH_2-CH=CH_2$[14], Oil, ^1H NMR:5.98—5.37(m,1 H),5.17—4.73(m,2 H),3.11—2.43(m,4 H),1.75—0.84(m,13 H),ppm; IR:2961,2890,1640,1483,1390,923,725,cm^{-1}.

6:n-$C_6H_{13}S-CH_2-CH=CH_2$[14], Oil, ^1H NMR:5.99—5.37(m,1 H),5.18—4.72(m,2 H),3.11—2.43(m,4 H),1.75—0.81(m,11 H),ppm; IR:2971,2897,1643,1481,1390,925,725,cm^{-1}.

7:$C_6H_5CH_2S-CH_2-CH=CH_2$[14], Oil, ^1H NMR:7.33—7.17(m,5 H),6.03—5.37(m,1 H),5.17—4.67(m,2 H),3.60—3.47(s,2 H),2.98—2.77(d,2 H),ppm; IR:3082,2960,1642,1512,1470,1080,923,745,698,cm^{-1}.

8:p-$ClC_6H_4CH_2S-CH_2-CH=CH_2$[14], Oil, ^1H NMR:7.40—7.25(m,4 H),6.05—5.40(m,1 H),5.20—4.75(m,2 H),3.68—3.38(s,2 H),3.01—2.80(d,2 H),ppm; IR:3086,2970,1645,1515,1472,1082,925,758,695,cm^{-1}.

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