

A novel synthesis of allyl and benzyl selenides *via* Sm/SbCl₃ system in aqueous media

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Allyl and benzyl selenides were synthesized *via* reactions of allyl and benzyl bromides and diselenides promoted by Sm/SbCl₃ system in aqueous media in moderate to good yields.

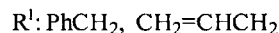
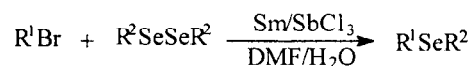
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Since the first Barbier-type reaction in aqueous media was reported in 1977,¹ organometallic reactions in aqueous media have attracted considerable attention in organic synthesis.²⁻⁵ If one can perform organometallic-type reactions in aqueous media just as generally and easily as in organic solvents, such reactions may offer considerable advantages: (1) there is the practical convenience of not having to handle inflammable and anhydrous organic solvents; (2) the tedious task of protection-deprotection chemistry for certain functional groups often encountered in organic synthesis may not be required; (3) water-soluble compounds can be reacted directly without the need of derivatization; (4) the regio and stereochemical outcomes of the reactions may well change from organic to aqueous media and this offers new opportunities in synthesis. This is a point of particular interest in carbohydrate chemistry. To date, the most commonly used metals in aqueous media were zinc, tin, indium and bismuth.²⁻⁶

Recently, many types of organometallic reactions were carried out in aqueous media.⁷ For example, aldimines could be reductively coupled by indium to vicinal diamines,⁸ α -bromoketones can react with carbonyl compounds to give β -hydroxy ketones at the promotion

of zinc or tin.⁹ We became interested in synthesis of selenides by organometallic reactions in aqueous media.¹⁰⁻¹²

The application of metallic antimony in organic synthesis has been studied.¹³⁻¹⁵ But in most cases, those reactions were carried out in nonaqueous condition. Recently, Ren and coworkers succeeded in allylation of aldehydes with SbCl₃/NaBH₄ in DMF/H₂O.¹⁶ Here we wish to report that allyl and benzyl bromides can react with diselenides promoted by Sm/SbCl₃ system in DMF/H₂O to give allyl and benzyl selenides under a nitrogen atmosphere.



The products and the reaction conditions are shown in Table 1. The yields are better under a nitrogen atmosphere. The reactions can be carried out in the air, but the yields are lower than that obtained under a nitrogen atmosphere (Entries 1, 6 and 12, 13). We examined the effects of several solvents and found the comparatively high yield was obtained from DMF/H₂O (4/1) system. (Entries 1, 6 and 16—19). We also examined the same reaction in DMF without water and observed a much slower reaction rate (Entries 1, 6 and 14, 15). It is noteworthy that a satisfactory yield of product could also be obtained when a catalytic amount of SbCl₃ was used (Entries 1—3 and 6—8), but this reaction did not take place in the absence of SbCl₃ or Sm powder.

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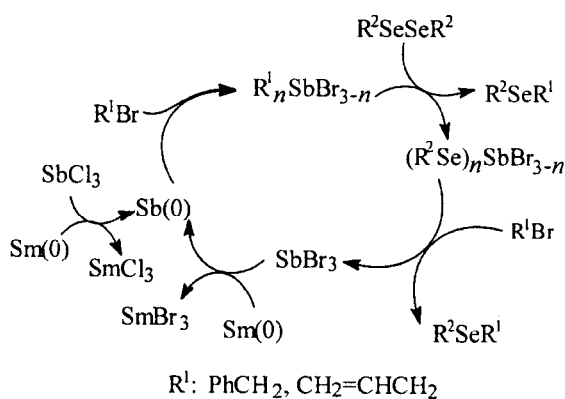
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Table 1 Reaction conditions and yield

Entry	R ¹	R ²	Reaction conditions				Yield (%) ^a
			Atmosphere	Solvent ^d	Temp. (°C)	Time (h)	
1	CH ₂ = CHCH ₂	Ph	N ₂	A	50	12	82
2	CH ₂ = CHCH ₂	Ph	N ₂	A	50	14	78 ^b
3	CH ₂ = CHCH ₂	Ph	N ₂	A	50	18	77 ^c
4	CH ₂ = CHCH ₂	<i>p</i> -ClC ₆ H ₄	N ₂	A	50	10	79
5	CH ₂ = CHCH ₂	<i>p</i> -CH ₃ C ₆ H ₄	N ₂	A	50	8	85
6	C ₆ H ₅ CH ₂	Ph	N ₂	A	60	8	86
7	C ₆ H ₅ CH ₂	Ph	N ₂	A	60	10	80 ^b
8	C ₆ H ₅ CH ₂	Ph	N ₂	A	60	16	78 ^c
9	C ₆ H ₅ CH ₂	<i>p</i> -ClC ₆ H ₄	N ₂	A	60	8	85
10	C ₆ H ₅ CH ₂	<i>n</i> -C ₄ H ₉	N ₂	A	60	18	54
11	C ₆ H ₅ CH ₂	C ₆ H ₅ CH ₂	N ₂	A	60	14	72
12	CH ₂ = CHCH ₂	Ph	Air	A	50	12	65
13	C ₆ H ₅ CH ₂	Ph	Air	A	60	10	58
14	CH ₂ = CHCH ₂	Ph	N ₂	B	50	20	80
15	C ₆ H ₅ CH ₂	Ph	N ₂	B	60	20	78
16	CH ₂ = CHCH ₂	Ph	N ₂	C	50	20	49
17	C ₆ H ₅ CH ₂	Ph	N ₂	C	60	20	53
18	CH ₂ = CHCH ₂	Ph	N ₂	D	50	18	54
19	CH ₂ = CHCH ₂	Ph	N ₂	E	50	20	0

a) Yield of isolated product is based on diselenides. Diselenides (0.5 mmol), allyl or benzyl bromide (1.5 mmol), Sm powder (2 mmol) and SbCl₃ (1 mmol) were employed. b) Diselenides (0.5 mmol), allyl or benzyl bromide (1.5 mmol), Sm powder (2 mmol) and SbCl₃ (0.2 mmol) were employed. c) Diselenides (0.5 mmol), allyl or benzyl bromide (1.5 mmol), Sm powder (2 mmol) and SbCl₃ (0.1 mmol) were employed. d) A. DMF/H₂O (4/1); B. DMF (anhydrous); C. THF (anhydrous); D. THF/H₂O (4/1); E. H₂O.

Cleavage of Se—Se bond can be achieved mainly by three routes:¹⁷ oxidative cleavage,^{18,19} nucleophilic assisted cleavage²⁰ and radical assisted cleavage.²¹ Although the reaction mechanism is not clear, a catalytic cycle can be presumed in which some allylantimony reagent is formed *via* proposed mechanism.²²



Selenides are useful synthetic reagents and inter-

mediates in organic synthesis.²³ Many synthetic methods *via* cleavage of Se—Se bond in diselenides have been reported. From a synthetic point of view, some major limitations of these reactions are: (1) the necessity to synthesize the organometallic complex; (2) loss of half unit of diselenides; (3) strong base catalysis, (4) the need for anhydrous organic solvents, *etc.*¹⁷ In contrast, the cleavage of Se—Se bond in diselenides by Sm/SbCl₃ system circumvents these problems. The present procedure provides a simple and easy alternative method for the synthesis of allyl and benzyl selenides in moderate to good yields.

Experimental

Melting points were uncorrected. IR spectra were recorded on a PE-683 spectrometer. ¹H NMR spectra were obtained with a JEOL PMX60si spectrometer in CCl₄ solution using TMS as internal standard. The reactions were performed under a nitrogen atmosphere.

General procedure

In a 50 mL three-neck flask fitted with a reflux condenser, were placed SbCl_3 (1 mmol), DMF (10 mL), Sm powder (2 mmol), benzyl and allyl bromide (1.5 mmol), H_2O (2.5 mL) and diselenides (0.5 mmol). The mixture was stirred at 50 or 60°C for given hours (see Table 1). The inorganic by-product was filtered off and washed with ether (3×10 mL). The combined ether-DMF solutions were then washed with brine (2×10 mL) and dried over magnesium sulfate. The solvent was evaporated *in vacuo* and the product was isolated by preparative TLC (silica gel) with cyclohexane as eluent.

Allyl phenyl selenide oil.²⁴ $\delta_{\text{H}}(\text{CCl}_4)$: 7.6—7.0(m, 5H), 6.0—5.4(m, 1H), 4.97—4.57(m, 2H), 3.53—3.13(d, $J = 7.0$ Hz, 2H). ν_{max} : 3090, 2942, 1644, 1590, 1482, 1440, 1180 cm^{-1} .

Allyl p-chlorophenyl selenide oil.²⁵ $\delta_{\text{H}}(\text{CCl}_4)$: 7.6—7.0(m, 4H), 6.0—5.5(m, 1H), 5.05—4.60(m, 2H), 3.55—3.10(d, $J = 7.2$ Hz, 2H). ν_{max} : 3100, 2943, 1645, 1580, 1480, 1442, 1200 cm^{-1} .

Allyl p-methylphenyl selenide oil.²⁵ $\delta_{\text{H}}(\text{CCl}_4)$: 7.5—6.8(m, 4H), 6.0—5.5(m, 1H), 5.00—4.47(m, 2H), 3.47—3.20(d, $J = 7.0$ Hz, 2H), 2.22(s, 3H). ν_{max} : 3080, 2965, 2870, 1642, 1510, 1380 cm^{-1} .

Benzyl phenyl selenide oil (Lit.,²⁶ 155°C/932 Pa). $\delta_{\text{H}}(\text{CCl}_4)$: 7.5—7.0(m, 10H), 3.94(s, 2H). ν_{max} : 3080, 3050, 3020, 2925, 1610, 1590, 1505, 1490, 1465, 1445, 1310, 1220 cm^{-1} .

Benzyl p-chlorophenylselenide mp 46—48°C (Lit.,²⁷ 43—45°C). $\delta_{\text{H}}(\text{CCl}_4)$: 7.4—6.9(m, 9H), 3.94(s, 2H). ν_{max} : 3105, 3080, 3060, 2955, 1605, 1505, 1485, 1460, 1400, 1220 cm^{-1} .

Benzyl n-butylselenide oil (Lit.,²⁶ 76°C/226 Pa). $\delta_{\text{H}}(\text{CCl}_4)$: 7.4—7.0(m, 5H), 3.66(s, 2H), 2.38(t, $J = 7.0$ Hz, 2H), 1.1—1.7(m, 4H), 0.86(t, $J = 6.0$ Hz, 3H). ν_{max} : 3105, 3080, 3050, 2980, 2890, 1612, 1595, 1505, 1472, 1462, 1380, 1265 cm^{-1} .

Dibenzyl selenide mp 44—46°C (Lit.²⁸, 45—45.5°C). $\delta_{\text{H}}(\text{CCl}_4)$: 7.17(s, 10H), 3.57(s, 4H). ν_{max} : 3105, 3080, 3050, 2950, 2880, 1610, 1595, 1508, 1463, 1425, 1220 cm^{-1} .

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