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A Novel Synthesis of Allyl Sulfides and Allyl Selenides *via* Sm–BiCl$_3$ System in Aqueous Media†

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Allyl sulfides and allyl selenides are synthesized *via* the reaction of allyl bromide with disulfides and diselenides promoted by the Sm–BiCl$_3$ system in aqueous media in moderate to good yields.

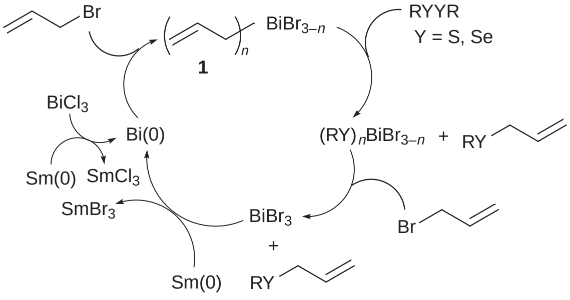
There has been considerable interest in performing organometallic reactions in aqueous media.[1] The most frequent reason changing organometallic reactions from strictly anhydrous organic solvents to aqueous media is the ease of reaction in obviating the need for inflammable anhydrous organic solvents and a troublesome inert atmosphere. For some reactions, *e.g.* alkylations of carbonyl group in carbohydrates, it is of great help that the substrates didn't need to be altered to suit their reaction in organic solvents.[2] The most commonly used metals are zinc, tin, indium and bismuth or BiCl$_3$–Al, BiCl$_3$–Zn and BiCl$_3$–Fe systems.[3]

However, the type of aqueous organometallic reactions seems to have been somewhat limited. It has been used mainly in Barbier-type reactions. We have become interested in other types of aqueous organometallic reaction, and to our knowledge no reaction mediated by bismuth has been used to prepare sulfides and selenides. As a part of our work in aqueous organometallic reactions, we wish to report here that allyl bromide can react with disulfides and diselenides promoted by Sm–BiCl$_3$ to give allyl sulfides and selenides.

The products and the reaction conditions are shown in the Table 1. The best yields are obtained under a nitrogen atmosphere. The reaction can be carried out in air, but the yields are lower than those obtained under a nitrogen atmosphere. We examined the effects of several solvents and found that comparatively high yields are obtained from THF–H$_2$O and DMF–H$_2$O systems.

$$CH_2{=}CH{-}CH_2{-}Br + RYYR \xrightarrow[THF–H_2O]{BiCl_3–Sm} CH_2{=}CH{-}CH_2YR$$

Cleavage of –S–S– and –Se–Se– bonds can be achieved by three major routes:[6] oxidative cleavage,[7] nucleophile-assisted cleavage[8] and radical-assisted cleavage.[9] Although the reaction mechanism of the catalytic BiCl$_3$-mediated cleavage is not clear, a catalytic cycle can be presumed in which some allylbismuth reagent **1** is prepared *via* the proposed mechanism[10] (Scheme 1).



Scheme 1 Proposed mechanism of catalytic BiCl$_3$–Sm(o) mediated reaction

Sulfides and selenides are useful synthetic reagents and intermediates in organic synthesis.[4,11] Many synthetic methods that involve cleavage of the –S–S– bond in sulfides and –Se–Se– bond in selenides have been reported. Most of them have some limitations.[6] For example, the necessity to synthesize the organometallic, loss of half-unit of disulfide and diselenide, strong base catalysis, the need for anhydrous organic solvents, *etc.* In contrast, the cleavage of –S–S– and –Se–Se– bonds by the Sm–BiCl$_3$ system circumvents these problems. The present procedure provides a simple and easy alternative method for the synthesis of sulfides and selenides in moderate to good yields.

Table 1 Reaction conditions and yields

Entry	Y	R	Solvent	Product	Atmosphere	Yield(%)	State
1	S	Ph	THF–H$_2$O(20/5)	PhSCH$_2$CH=CH$_2$	N$_2$	87	Oil[4]
2	S	Ph	THF–H$_2$O(20/5)	PhSCH$_2$CH=CH$_2$	Air	47	
3	S	Ph	DMF–H$_2$O(20/5)	PhSCH$_2$CH=CH$_2$	N$_2$	83	
4	S	*p*-CH$_3$C$_6$H$_4$	THF–H$_2$O(20/5)	*p*-CH$_3$C$_6$H$_4$SCH$_2$CH = CH$_2$	N$_2$	84	Oil[4]
5	S	*p*-ClC$_6$H$_4$	THF–H$_2$O(20/5)	*p*-ClC$_6$H$_4$SCH$_2$CH = CH$_2$	N$_2$	85	Oil[4]
6	S	PhCH$_2$	THF–H$_2$O(20/5)	PhCH$_2$SCH$_2$CH = CH$_2$	N$_2$	71	Oil[4]
7	Se	Ph	THF–H$_2$O(20/5)	PhSeCH$_2$CH = CH$_2$	N$_2$	77	Oil[5]
8	Se	Ph	THF–H$_2$O(20/5)	PhSeCH$_2$CH = CH$_2$	Air	56	
9	Se	Ph	DMF–H$_2$O(20/5)	PhSeCH$_2$CH = CH$_2$	N$_2$	90	
10	Se	*p*-CH$_3$C$_6$H$_4$	THF–H$_2$O(20/5)	*p*-CH$_3$C$_6$H$_4$SeCH$_2$CH = CH$_2$	N$_2$	82	Oil[5]
11	Se	*p*-ClC$_6$H$_4$	THF–H$_2$O(20/5)	*p*-ClC$_6$H$_4$SeCH$_2$CH = CH$_2$	N$_2$	80	Oil[5]
12	Se	*n*-C$_4$H$_9$	THF–H$_2$O(20/5)	*n*-C$_4$H$_9$SeCH$_2$CH = CH$_2$	N$_2$	69	Oil[5]
13	Se	*n*-C$_4$H$_9$	DMF–H$_2$O(20/5)	*n*-C$_4$H$_9$SeCH$_2$CH = CH$_2$	N$_2$	75	

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Experimental

Typical Procedure.—In a 50 ml three-neck flask fitted with a reflux condenser, are placed Sm powder (0.3 g), $BiCl_3$ (1 mmol), allylic bromide (1.5 mmol) and disulfides (0.5 mmol) or diselenides (0.5 mmol). The mixture was stirred at 60 °C for 12 h. It was extracted with Et_2O. After drying (Na_2SO_4), the solvent was evaporated *in vacuo* and the product was isolated by preparative TLC on silica gel using light petroleum (bp 30–60 °C) as eluent. The products were characterized by their ^1H NMR and IR spectra.

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References

1 For reviews see (*a*) C. J. Li, *Chem. Rev*., 1993, **93**, 2023; (*b*) A. Lubineau, J. Auge and Y. Queneau, *Synthesis*, 1994, 741.
2 C. J. Li and T. H. Chan, *Tetrahedron Lett.,* 1991, 32, 7017.
3 A. R. Katritzky, N. Shobana and P. A. Harris, *Organometallics*, 1992, **11**, 1381.
4 Yu Mingxin and Zhang Yongmin, *Synth. Commun*., 1997, **27** 2743.
5 Yu Mingxin and Zhang Yongmin, *Synth. Commun*., 1997, **27**, 609.
6 S. Chowdhury and S. Roy, *Tetrahedron Lett*., 1997, **38**, 2149.
7 (*a*) R. Kumar, H. E. Mabrouk and D. G. Tuck, *J. Chem. Soc., Dalton Trans*., 1988, **4**, 1045; (*b*) Y. Taniguchi, M. Marou and K. Takaki, *Tetrahedron Lett*., 1994, **35**, 7789.
8 S. T. Kobanyane and D. I. Majee, *Can. J. Chem*., 1992, **70**, 2758.
9 I. Das and S. Roy, *J. Organomet. Chem*., 1994, **467**, 223.
10 M. Wada and H. Ohki, *Bull. Chem. Soc. Jpn*., 1990, **63**, 1738.
11 S. Halazy and A. Kriet, *Tetrahedron Lett*., 1981, **22**, 2135.