This article was downloaded by: [North Dakota State University] On: 13 December 2014, At: 19:02 Publisher: Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/lsyc20

A Novel Synthesis of Benzyl Sulfides and Selenides via Sm/BiCl₃ System in Aqueous Media

Genliang Lu^a & Yongmin Zhang^a ^a Department of Chemistry, Hangzhou University, Hangzhou, 310028, P.R. China Published online: 23 Aug 2006.

To cite this article: Genliang Lu & Yongmin Zhang (1998) A Novel Synthesis of Benzyl Sulfides and Selenides via Sm/BiCl₃ System in Aqueous Media, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 28:23, 4479-4484, DOI: <u>10.1080/00397919808004483</u>

To link to this article: http://dx.doi.org/10.1080/00397919808004483

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

A NOVEL SYNTHESIS OF BENZYL SULFIDES AND SELENIDES VIA Sm/BiCl₃ SYSTEM IN AQUEOUS MEDIA

Genliang Lu and Yongmin Zhang*

Department of Chemistry, Hangzhou University Hangzhou, 310028, P.R.China

Abstract: Benzyl sulfides and selenides are synthesized via reaction of benzyl bromide with disulfides and diselenides promted by Sm/BiCl₃ system in aqueous media in moderate to good yields.

Recently, organometallic-type reactions in aqueous media have attracted considerable interest in organic synthesis.¹ Such reactions in aqueous media offer a number of advantages over conventional organometallic reactions in organic solvents: (1) There is the practical convenience, and possible environmental benefits, of not having to use inflammable and anhydrous organic solvents; (2) The tedious task of protection-deprotection chemistry for certain functional groups often encountered in organic synthesis may be obviated; (3) Water-soluble compounds such as carbohydrates can be reacted directly without the need of derivatization.

^{*} To whom correspondence should be addressed.

The most commonly used metals are zinc, indium, tin and bismuth or BiCl₃-Al, BiCl₃-Zn and BiCl₃-Fe systems.^{1,2}

However, the type of the aqueous organometallic reactions seems to have been somewhat limited. It has been used mainly in allylation and propargylation of carbonyl compounds. We became interested in other type of the aqueous organometallic reaction. To our knowledge, no reaction mediated by bismuth is used to prepare the sulfides and selenides. As a part of our work in aqueous organometallic reactions, here we wish to report that benzyl bromide can react with disulfides and diselenides promted by Sm/BiCl₃ system to give benzyl sulfides and benzyl selenides. The products and the reaction conditions are shown in the Table. We examined the effects of several solvents and found the comparatively high yields are obtained from THF/H₂O and DMF/H₂O systems.

Sulfides and selenides are useful synthetic reagents and intermediates in organic synthesis.³ Many synthetic methods via cleavage of S-S bond in disulfides and 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 disulfide and diselenide, (3) strong base catalysis, (4) the need for anhydrous organic solvents, etc.⁴ In contrast, the cleavage of S-S bond in disulfides and Se-Se bond in diselenides by Sm/BiCl₃ system circumvents these problems. The present procedure provides a simple and

Scheme

PhCH₂Br + RZZR $\xrightarrow{Sm/BiCl_3}$ PhCH₂ZR THF/H₂O or DMF/H₂O Z=S, Se.

Entry	Z	R	Solvents	Time(h)	Product	Yield*(%)
1	S	Ph	THF/H ₂ O(4/1)	5	PhCH ₂ SPh	70
2	S	Ph	DMF/H ₂ O(4/1)	5	PhCH ₂ SPh	75
3	S	PhCH ₂	THF/H ₂ O(4/1)	5	PhCH ₂ SCH ₂ Ph	75
4	Se	Ph	THF/H ₂ O(4/1)	6	PhCH ₂ SePh	84
5	Se	Ph	DMF/H ₂ O(4/1)	5	PhCH ₂ SePh	81
6	Se	p-ClC ₆ H ₄	THF/H ₂ O(4/1)	8	PhCH ₂ SeC ₆ H ₄ Cl-p	82
7	Se	p-ClC ₆ H ₄	DMF/H ₂ O(4/1)	8	PhCH ₂ SeC ₆ H ₄ Cl-p	82
8	Se	PhCH ₂	THF/H ₂ O(4/1)	5	PhCH ₂ SeCH ₂ Ph	73
9	Se	n-C₄H9	THF/H ₂ O(4/1)	5	PhCH ₂ SeC ₄ H ₉ -n	84

Table Reaction Conditions and Yield.

*Yield of Isolated Product on disulfides or diselenides.

easy alternative method for the synthesis of benzyl sulfides and benzyl selenides in moderate to good yields.

Experimental Section

Melting points were uncorrected. IR spectra were recorded on a PE-683 spectrometer, ¹H NMR spectra were obtained with a Bruker 80 spectrometer in

CCl₄ solution using TMS as internal standard. The reactions were performed in a Schlenk type glass apparatus under a nitrogen atmosphere.

General Procedure

In a 50 mL three-neck flask fitted with a reflux condenser, were placed BiCl₃ (1mmol), THF or DMF (10mL), Sm power (2mmol), benzyl bromide (1.5mmol), H₂O (2.5mL) and disulfides or diselenides (0.5mmol). The mixture was stirred at 60°C for a given hours (see Table). The inorganic by-product was filtered off and washed with ether (3×10 mL). The combined ether-THF 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 preprative TLC (silica gel) with cyclohexane as eluent.

Benzyl phenyl sulfide: m.p.40-42°C (lit⁵, 40-41°C); ¹H NMR, 7.4-6.9 (m, 10H), 3.97 (s, 2H) ppm; IR, 3100, 3080, 3050, 2925, 1600, 1575, 1505, 1490, 1460, 1448, 1245, 1090, 1070, 1028, cm⁻¹.

Dibenzyl sulfide: m.p. 48-50°C (lit⁵, 49°C); ¹H NMR, 7.17 (s, 10H), 3.45 (s, 4H) ppm; IR, 3110, 3080, 3050, 2940, 1625, 1600, 1505, 1462, 1430, 1232, 1205, 1070, 1030, cm⁻¹.

Benzyl phenyl selenide: oil (lit⁶, 155°C/7mmHg); ¹H NMR, 7.5-7.0 (m, 10H), 3.97 (s, 2H) ppm; IR, 3080, 3040, 3020, 2950, 1610, 1590, 1505, 1485, 1465,

1445, 1310, 1220, 1185, 1160, 1075, 1025, 1002, cm⁻¹.

Benzyl p-chlorophenyl selenide: m.p. 44-46°C (lit⁷, 43-45°C); ¹H NMR, 7.4-6.9 (m, 9H), 3.94 (s, 2H) ppm; IR, 3105, 3080, 3060, 2955, 1605, 1505, 1485, 1460, 1400, 1220, 1180, 1110, 1100, 1070, 1030, 1010, cm⁻¹.

Dibenzyl selenide: m.p. 44-46°C (lit⁸, 45-45.5°C); ¹H NMR, 7.17 (s, 10H), 3.57 (s, 4H); IR, 3105, 3080, 3050, 2950, 2880, 1610, 1595, 1508, 1463, 1425,1220,1182,1070, 1030, cm⁻¹.

Benzyl n-butyl selenide: oil (lit⁶, 76°C/2mmHg); ¹H NMR, 7.4-7.0 (m, 5H), 3.67 (s, 2H), 2.38 (t, 2H), 1.1-1.7 (m, 4H), 0.86 (t, 3H); IR, 3105, 3080, 3050, 2980, 2970, 2890, 1612, 1595, 1505, 1472, 1462, 1380, 1265, 1190, 1070, 1030, cm⁻¹.

Acknowledgement

We thank the National Natural Science Foundation of China (Project No. 29672007 and 294938004) and the Lababortory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences for financial support.

References

1. (a) Chan, T.H.; Li, C.J.; Lee, M.C.; Wei, Z.Y. Can. J. Chem., 1994, 72, 1181;

(b) Li, C.J. Chem. Rev., 1993, 93,2023; (c) Lubineau, A.; Auge, J.; Queneau,
Y. Synthesis, 1994, 741; (d) Chan, T.H.; Isaac, M.B. Pure & Appl. Chem.,
1996, 68, 919.

- 2. Katritzky, A.R.; Shobana, N.; Harris, P.A. Organometallics, 1992, 11, 1381.
- (a) Yu, M.X.; Zhang, Y.M. Synth. Commun., 1997, 27, 2743; (b) Patai, S.; Rappoport, Z. (eds): The Chemistry of Organic Selenium and Tellurium Compounds, Vol. 1, Wiley, Chichester, 1986.
- 4. Chowdhury, S.; Roy, S. Tetrahedron Lett., 1997, 38, 2149.
- 5. Shriner, R.L.; Struck, H.C.; Jorison, W. J. J. Am. Chem. Soc., 1930, 52, 2060.
- 6. Okamoto, Y.; Yano, T. J. Organometal. Chem., 1971, 29,99.
- Comasseto, J.V.; Lang, E.S.; Tercio, J.; Ferreira, B.; Simonelli, F.; Correia, V.R. J. Organomet. Chem., 1987, 334, 329.
- 8. Otsuba, J.; Ogura, F. Synth. Commun., 1980, 10, 595.

(Received in the U.S.A. 08 June 1998)