This article was downloaded by: [Carnegie Mellon University] On: 09 November 2014, At: 02:36 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

The Synthesis of Allyl Selenides by Organosamarium Reagent

Mingxin Yu^a, Yongmin Zhang^a & Weiliang Bao^a ^a Department of Chemistry, Hangzhou University, Hangzhou, 310028, P.R. China Published online: 20 Aug 2006.

To cite this article: Mingxin Yu, Yongmin Zhang & Weiliang Bao (1997) The Synthesis of Allyl Selenides by Organosamarium Reagent, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 27:4, 609-613, DOI: <u>10.1080/00397919708003332</u>

To link to this article: http://dx.doi.org/10.1080/00397919708003332

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

THE SYNTHESIS OF ALLYL SELENIDES BY ORGANOSAMARIUM REAGENT

Mingxin Yu, Yongmin Zhang*, Weiliang Bao

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

Abstract: Organosamarium reagent reacts with diselenides to afford allyl selenides in THF.

The intensive studies have been carried out on the SmI_2 in organic synthesis^{1,2,3}. However, studies on application of samarium metal in organic synthesis were very few^{4,5}. Curran firstly reported the samarium Grignard reaction⁶. Our group have studied the synthesis of symmetric and asymmetric selenides (or diselenides) by SmI₂^{7,8} and reaction of organosamarium reagent with imine⁹. Allyl selenides are very important intermediates in organic synthesis. Many rearrangement reactions of allyl selenides can be taken place, for example, (3,3) sigmatrapic rearrangement leads to heterocyclic compound containing selenium¹⁰. Substitution reactions of allyl selenides can be undergone with a variety of typical electrophiles¹¹. Allyl selenides also cause reductive allylic homocoupling in the presence of the catalyst¹². Diels-Alder reactions of allyl selenides can be occurred to give cyclized compounds¹³. Oxidation reactions of allyl selenides may be carried out, then a rearrangement leads to carbon-oxygen bond compound¹⁴. Allylic selenium ylides are effective reagents for synthesizing new compounds

containing substituent on carbon¹⁵. Therefoe, the synthesis of allyl selenides is very significant. Kataev, E. G.¹⁶ described that sodium reacted with selenophenol in absolute ethanol at low temperature, then was added allyl bromide drop by drop to give allyl selenides. Hori¹⁷ reported that diphenyl diselenide reacted with sodium borohydride to form sodium salt of selenophenol in absolute ethanol under nitrogen. The reaction mixture was stirred at room temperature for 5h to give allyl selenides. Herein we wish to report the synthesis of allyl selenides by reaction of organosamarium reagent with diselenides in THF. The results were summarized in table 1.

$$CH_2 = CH - CH_2Br + Sm - \frac{THF}{rt} CH_2 = CH - CH_2SmBr$$

$$CH_2 = CH - CH_2SmBr + RSeSeR \frac{THF}{rt. or reflux} CH_2 = CH - CH_2SeR$$

Laber 1. Acadion Conditions and Trend				
No.	Product	Reaction	Reaction	Yield*
		Time(h)	Temp.(°C)	(%)
1	C ₆ H ₅ SeCH ₂ CH=CH ₂	1	r.t.	80
2	p-ClC ₆ H ₄ SeCH ₂ CH=CH ₂	1	r.t.	82
3	p-CH ₃ C ₆ H ₄ SeCH ₂ CH=CH ₂	1	r.t.	81
4	o-CH ₃ C ₆ H ₄ SeCH ₂ CH=CH ₂	1	r.t.	78
5	CH ₃ (CH ₂) ₅ SeCH ₂ CH=CH ₂	1	reflux	64
6	CH ₃ (CH ₂) ₃ SeCH ₂ CH=CH ₂	1	reflux	61
7	CH ₃ CH ₂ CH(CH ₃)SeCH ₂ CH=CH ₂	1	reflux	58
8	CH ₃ CH ₂ SeCH ₂ CH=CH ₂	1	reflux	57

Table 1. Reaction Conditions and Yield

* Yield of isolated product

The advantages of this method are simple operation, mild and neutral conditions, as well as good yield.

Experimental

Tetrahydrofuran was distilled from sodium/benzophenone ketyl immediately before use. Elemental analyses were carried out using a Carlo Erba 1106 instrument. IR spectra were recorded on a PE 683 spectrometer. ¹H NMR spectra were obtained with a JEOL PMX60si spectrometer in CCl_4 solution using TMS as internal standard.

General procedure for the synthesis of allyl selenides: 0.33g (2.2mmol) samarium and 20mL THF, 0.30g (2.5mmol) allyl bromide were added to athree necked flask with stirring at room temperature under nitrogen. When the mixture became purple, then continue to stir for 1h until the samarium powder disappear. Diselenide was then added to the solution, and the mixture was stirred for 1h at room temperature (or reflux) under nitrogen. The reaction mixture was extracted with ether ($40mL \times 3$) and the ether layer was seperated. The etheral solution was washed with water ($40mL \times 2$), dried over MgSO₄. The solvents were removed by evaporation under reduced pressure. The crude product was purified by preparative TLC on silica gel (cyclohexane and ethyl acetate as eluent). The products were identified by elemental analyses, IR and ¹H NMR spectra.

C₆H₅SeCH₂CH=CH₂¹⁶: oil, IR(film): 3090, 2942, 1644, 1486, 1180, 998, 912, 730, 682cm⁻¹, ¹H NMR: 7.60-6.97(m, 5H), 5.93-5.53(m, 1H), 4.97-4.57(d, 2H), 3.45-3.17(d, 2H).

p-ClC₆H₄SeCH₂CH=CH₂¹⁷: oil, IR(film): 3110, 2950, 1648, 1480, 1180, 1090, 1004, 820, 685cm⁻¹, ¹H NMR: 7.57-6.93(m, 4H), 5.93-5.56(m, 1H), 5.10-4.60(d, 2H), 3.60-3.20(d, 2H).

p-CH₃C₆H₄SeCH₂CH=CH₂¹⁶: oil, IR(film): 3080, 2965, 2870, 1642, 1510, 1380, 990, 830cm-1, ¹H NMR: 7.50-6.73(m, 4H), 5.90-5.53(m, 1H), 5.00-4.53(d, 2H), 3.43-3.19(d, 2H), 2.33-2.10(s, 3H).

o-CH₃C₆H₄SeCH₂CH=CH₂: oil, IR(film): 3070, 2960, 1640, 1512, 1380, 994, 908, 832cm-1, ¹H NMR: 7.60-6.73(m, 4H), 5.97-5.57(m, 1H), 5.03-4.63(d, 2H), 3.43-3.17(d, 2H), 2.43-2.23(s, 3H). Anal. Calad. for C₁₀H₁₂Se: C 56.88, H 5.728, found: C 56.76, H 5.681.

 $CH_3(CH_2)_5SeCH_2CH=CH_2$: oil, IR(film): 2956, 2866, 1640, 1185, 992, 885, 760cm⁻¹; ¹H NMR: 5.93-5.53(m, 1H), 5.05-4.60(d, 2H), 2.90-3.47(m, 4H), 0.96-1.72(m, 11H). Anal. Calad. for $C_9H_{18}Se$: C 52.68, H 8.842, found: C 52.53, H 8.763.

 $CH_3(CH_2)_3SeCH_2CH=CH_2$: oil, IR(film): 2962, 2930, 2884, 1642, 1468, 1318, 992, 910cm⁻¹; ¹H NMR: 5.90-5.53(m, 1H), 5.00-4.58(d, 2H), 3.43-3.17(d, 2H), 3.00-2.70(m, 2H), 0.98-1.68(m, 7H). Anal. Calad. for $C_7H_{14}Se$: C 47.46, H 7.966, found: C 47.28, H 7.901.

CH₃CH₂CH(CH₃)SeCH₂CH=CH₂: oil, IR(film): 2966, 2932, 2880, 1642, 1380, 1140, 995cm-1; ¹H NMR: 5.93-5.50(m, 1H), 5.03-4.56(d, 2H), 3.40-2.75(m, 3H), 0.97-1.63(m, 8H); Anal. Calad. for C_7H_{14} Se: C 47.46, H 7.966, found: C 47.32, H 7.884.

CH₃CH₂SeCH₂CH=CH₂: oil, IR(film): 2964, 2935, 2860, 1640, 1210, 1160, 992, 908cm-1; ¹H NMR: 5.90-5.50(m, 1H), 4.98-4.55(d, 2H), 3.50-3.16(m, 4H), 1.26-1.48(t, 3H); Anal. Calad. for C₅H₁₀Se: C 40.28, H 6.761, found: C 40.14, H 6.682.

Acknowledgement

We thank the National Natural Science Foundation of China and the Laboratory of Organometallic Chemistry, Shanghai Institue of Organic Chemistry, Chinese Academy of Sciences for financial support.

References

- 1. Girard, P., Namy, J. L., Kagan, H. B., J. Am. Chem. Soc., 1980, 102, 2693.
- 2. Molender, G. A., Chem. Rev., 1992, 92, 29.
- 3. Lin, R., Chen, L., Zhang, Y., Youji Huaxue, 1989, 9, 300.
- 4. Molender, G. A., Etter, J. B., J. Org. Chem., 1986, 51, 1778; 1987, 52, 3942.
- 5. Fukuzawa, S., Fujinami, S., J. Chem. Soc. Chem. Commun., 1986, 475.
- Dennis, P., Curran and Michael J. Totleben, J. Am. Chem. Soc., 1992, 114, 6050.
- 7. a). Zhang, Y. M., Jia, X. S., Zhou, X. J., Org. Pre. Pro. Intern., 1993, 25, 681.

- b). Zhang, Y. M., Jia, X. S., Zhou, X. J., Synth. Commun., 1994, 24, 1247.
- c). Jia, X. S., Zhang, Y. M., Zhou, X. J., Synth. Commun., 1993, 23, 1403.
- 8. a). Bao, W. L., Zhang, Y. M., Chen, S. W., Synth. Commun., 1994, 24, 1339.
 b). Zhang, Y. M., Yu, Y. P., Lin, R. H., Synth. Commun., 1993, 23, 189.
- 9. Wang, J. Q., Zhang, Y. M., Synth. Commun., in press.
- 10. Chmutova, G. A., et al, Kim. Geol., 1967, 706.
- Spaltenstein, A., Carpiro, P. A., Miyoke, F., Hopkims, P. B., J. Org. Chem., 1987, 52, 3759.
- Masugama, Y., Yamada, K., Shimizu, S., Bull. Chem. Soc. Jpn., 1989, 62, 2913.
- 13. Roger, M., Danil, B., Helv. Chim. Acta., 1978, 61, 3096.
- Reich, H. J., Yelm, K. E., Susan Wollowitz, J. Am. Chem. Soc., 1983, 105, 2503.
- 15. Halazy, S., Kriet, A., Tetrahedron Lett., 1981, 22, 2135.
- a). Kataev, E. G., Kataeva, L. M., Chmutova, G. A., *Zh. Org. Khim.*, 1966, 2, 2244.
 - b). Kataev, E. G., Chmutova, G. A., Yarkova, E. G., Plotnikova, T. G., Zh. Org. Khim., 1969, 5, 1514.
- 17. Hori, T., Sharpless, K. B., J. Org. Chem., 1979, 44, 4208.

(Received in the UK 3rd July 1996)

Downloaded by [Carnegie Mellon University] at 02:36 09 November 2014