This article was downloaded by: [North Carolina State University] On: 29 March 2015, At: 09:26 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

Synthesis of α-Benzotriazole Selenides and Tellurides Promoted by Samarium Diiodide

Jianqing Zhou^a, Weiliang Bao^a, Yongmin Zhang^a & Junquan Wang^a

^a Department of Chemistry, Hangzhou University, Hangzhou, 310028, P. R. China Published online: 21 Aug 2006.

To cite this article: Jianqing Zhou , Weiliang Bao , Yongmin Zhang & Junquan Wang (1996) Synthesis of α -Benzotriazole Selenides and Tellurides Promoted by Samarium Diiodide, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 26:17, 3283-3288, DOI: 10.1080/00397919608004638

To link to this article: http://dx.doi.org/10.1080/00397919608004638

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

SYNTHESIS OF α - BENZOTRIAZOLE SELENIDES AND TELLURIDES PROMOTED BY SAMARIUM DIIODIDE

Jianqing Zhou, Weiliang Bao, Yongmin Zhang*, Junquan Wang Department of Chemistry, Hangzhou University, Hangzhou, 310028, P.R.China

Abstract: 1-(Benzotriazol-1-yl) unsymmetrical diorganyl selenides and tellurides were synthesized via replacement of chlorine atom in 1-(benzotriazo-1-yl)-1-chloromethane with selenolate and tellurolate anions promoted by SmI₂.

Diorganyl selenides and diorganyl tellurides are important organoselenium and tellurium compounds¹. Furthermore, some other selenium and tellurium compounds, such as triorganyl selenonium halides, diorganyl tellurium dihalides, can be synthesized from diorganyl selenides and diorganyl tellurides². It has recently been found that selenolate anion (RSeSmI₂) and tellurolate anion (RTeSmI₂) obtained from reductive cleavage of diorganyl selenides and tellurides with samarium diiodide are powerful nucleophilic reagents. Some interesting reaction have taken place with them³. The most interesting reactions caused by RSeSmI₂ or RTeSmI₂ are the aromatic nucleophilic substitution and the six membered ring opening of isopropylidene malonate derivatives^{3c,3d,3e}. Here we wish to report that these alkylselenolate anion of the samarium salts can easily displace chlorine atom in 1-(benzotriazol-1-yl)-1-chloromethane to form 1-(benzotriazol-1-yl) unsymmetrical diorganyl selenides:

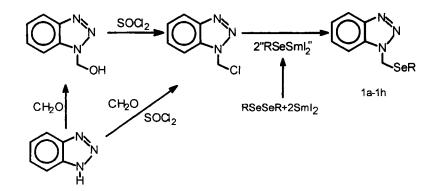
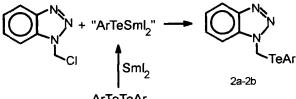


Table 1 1-(Denzouriazoi-1-yr) Selenides						
Entry	R	m.p.	Reaction	Yield		
		(°C)	Time(h)	(%)		
la	СН ₂ СН ₃	49-51	6	80		
1b	Сн ₂ Сн ₃ Сн ₂ СнСн ₃ Сн ₃	68-70	6	78		
lc	(CH ₂) ₃ CH ₃	oil	6	82		
Id	(CH ₂) ₄ CH ₃	oil	6	81		
le	(CH ₂) ₅ CH ₃	oil	6	80		
1f	\bigcirc -	86-88	8	75		
1g	ci -	110-112	8	72		
lh	\bigcirc	66-68	8	76		

 Table 1
 1-(Benzotriazol-1-yl) Selenides

Similarly, samarium aryltellurolate anion can also condense with 1-(benzotriazol-1-yl) -1-chloromethane to form corresponding tellurium



ArTeTeAr

Entry	R	m.p.(°C)	Reaction	Yield
			<u>Ti</u> me(h)	(%)
2a	\bigcirc	123-125	5	80
2b	СНз-	112-114	5	83

Table 2 1-(Benzotriazol-1-yl) Tellurides

The reactions were carried out at room temperatures. The starting material are easy to prepare⁴. The products containing benzotriazole at 1-position to the selenium or tellurium atom may subject further reactions and become another α -functionallized selenides or tellurides, for benzotriazole is a novel synthetic auxiliary and can be substituted by a number of nucleophiles⁵.

EXPERIMENTAL

¹H-NMR spectra were recorded in $CDCl_3$ on JEOL PMX 60si spectrometer using TMS as internal standard. IR spectra were obtained on a PE 683 spectrometer. Melting points are reported uncorrected. 1-(benzotriazol-1-yl)chloromethane is prepared according to reference 4. Sml₂ is prepared by samarium and iodine in dried THF. All the solvents used were predried according to standard procedures.

The reaction were performed in a Schlenk type glass apparatus and under a nitrogen atmosphere.

General procedure for the preparation of 1-(benzotriazol-1-yl) unsymmetrical diorganyl selenides:

To a solution of SmI_2 (2.1mmol, in 20ml THF), 1mmol diselenide and 0.5ml HMPA are added. After stirred for 3hrs at room temperatures, 2mmol of 1-(benzotriazol-1-yl)chloromethane is added and reacted for given hrs. The reaction mixture is treated with dilute hydrochloric acid (0.1M, 1ml) and extracted with ether twice. Organic phase is worked-up as usual and the product is seperated by preparative TLC (silica gel) with cyclohexane and ethyl acetate (8:1) as eluent.

1a: ¹H NMR(CDCl₃): 1.33(t, 3H, CH₃, J=6.8Hz), 2.62(q, 2H, SeCH₂, J=6.8Hz), 5.78(s, 2H, NCH₂), 7.23-7.62(m, 3H, ArH), 7.97-8.12(m, 1H, ArH); IR: 3080, 3025, 2980, 2940, 1625, 1605, 1505, 1462, 1315, 1225, 1165, 1075, 928, 780, 740, 625, 600cm⁻¹.

1b: ¹H NMR(CDCl₃): 0.89(d, 6H, CH₃, J=6.6Hz), 1.23-1.77(m, 1H), 2.57(d, 2H, SeCH₂, J=7.2Hz), 5.77(s, 2H, NCH₂), 7.27-7.67(m, 3H, ArH), 7.98-8.17(m, 1H, ArH); IR: 3100, 3060, 3020, 2970, 2940, 2885, 1625, 1603, 1505, 1462, 1370, 1310, 1265, 1230, 1220, 1163, 1065, 925, 845, 775, 740, 660, 620cm⁻¹.

1c: ¹H NMR(CCl₄): 0.87(t, 3H, CH₃, J=6Hz), 1.18-1.72(m, 4H), 2.59(t, 2H, SeCH₂, J=6.6Hz), 5.72(s, 2H, NCH₂), 7.27-7.60(m, 3H, ArH), 7.91-8.07(m, 1H, ArH); IR (neat): 3085, 3030, 2980, 2950, 2890, 1625, 1603, 1504, 1462, 1310, 1290, 1265, 1250, 1225, 1160, 1050, 1002, 925, 835, 775, 740, 660, 620cm⁻¹.

ld: ¹H NMR(CCl₄): 0.84(t, 3H, CH₃, J=5.6Hz), 1.13-1.73(m,6H), 2.58(t, 2H, SeCH₂, J=6.2Hz), 5.73(s, 2H, NCH₂), 7.23-7.62(m, 3H, ArH), 7.93-8.09(m, 1H, ArH); IR (neat): 3090, 3030, 2980, 2950, 2890, 2880, 1625, 1603, 1505, 1462,

1310, 1290, 1266, 1245, 1225, 1160, 1050, 1002, 924, 840, 775, 740, 660, 620cm⁻¹.

1e: ¹H NMR(CCl₄): 0.80-1.71(m, 11H), 2.60(t, 2H, SeCH₂, J=6.2Hz), 5.72(s, 2H, NCH₂), 7.23-7.62(m, 3H, ArH), 7.92-8.15(m, 1H, ArH); IR(neat): 3085, 3030, 2980, 2950, 2890, 2870, 1626, 1603, 1504, 1475, 1460, 1425, 1400, 1385, 1310, 1288, 1265, 1250, 1225, 1198, 1160, 1135, 1115, 1050, 1002, 924, 835, 775, 740, 660, 618, 600cm⁻¹.

1f: ¹H NMR(CDCl₃): 6.02(s, 2H), 7.20-7.49(m, 8H), 7.98-8.15(m, 1H); IR: 3120, 3098, 3080, 3030, 2975, 1625, 1602, 1590, 1503, 1484, 1460, 1445, 1432, 1402, 1318, 1296, 1270, 1252, 1225, 1165, 1135, 1080, 1070, 1021, 1000, 925, 850, 775, 765, 750, 740, 730, 685, 610cm⁻¹.

lg: ¹H NMR(CDCl₃): 5.96(s, 2H, NCH₂), 7.06-7.50(m, 7H), 7.95-8.11(m, 1H); IR: 3090, 3055, 3030, 2980, 2940, 2870, 1625, 1602, 1502, 1485, 1460, 1430, 1398, 1385, 1315, 1305, 1292, 1270, 1260, 1228, 1165, 1160, 1135, 1090, 1070, 1010, 945, 835, 815, 775, 740, 690, 660, 610cm⁻¹.

1h: ¹H NMR(CDCl₃): 1.43(m, 10H), 2.86-3.13(m, 1H), 5.85(s, 2H, NCH₂), 7.33-7.75(m, 3H, ArH), 8.03-8.19(m, 1H, ArH); IR: 3090, 3030, 2950, 2870, 1625, 1603, 1504, 1458, 1472, 1400, 1313, 1288, 1270, 1255, 1220, 1185, 1160, 1135, 1105, 1065, 995, 975, 885, 845, 775, 763, 740cm⁻¹.

2a: ¹H NMR(CDCl₃): 6.16(s, 2H, NCH₂), 7.13-7.47(m, 6H), 7.99-8.13(m, 1H); IR: 3090, 3070, 3035, 2970, 1627, 1618, 1600, 1585, 1504, 1480, 1460, 1440, 1425, 1405, 1316, 1290, 1270, 1230, 1200, 1165, 1140, 1060, 1020, 1000, 925, 800, 765, 750, 735, 725, 685, 590cm⁻¹.

2b: ¹H NMR(CDCl₃): 2.30(s, 3H, CH₃), 6.12(s, 2H, NCH₂), 6.97(d, 2H), 7.18-7.61(m, 5H), 7.94-8.08(m, 1H); IR: 3110, 3085, 3035, 2970, 2930, 2880, 1625, 1600, 1505, 1495, 1460, 1420, 1404, 1320, 1310, 1285, 1235, 1200, 1165, 1135, 1060, 1015, 925, 795, 790, 760, 745, 735, 590cm⁻¹. ACKNOWLEDGEMENTS: We thank the National Science Foundation of China and Academia Sinica for financial supports.

REFERENCES

- 1. Patai, S.and Rappoport, 2(eds), *The Chemistry of Organic Selenium and Tellurium Compounds*, Vol. 1, Wiley, Chichester, **1993**.
- 2. a). Wynne, K.J., George, J.W., J. Amer. Chem. Soc., 1969, 91, 1649.
 - b). Piette, J.L., Renson, M., Bull. Soc. Chim. Belges., 1970, 79, 353.
- 3. a). Fukuazawa, S., Niimoto, Y., Fujinami, T., Sakai, S., *Heteroatom* Chemistry, **1990**, 491.
 - b). Zhang, Y.M., Yu, Y.P., Lin, R., Synth. Commun., 1993, 23, 189.
 - c). Bao, W.L., Zhang, Y.M., Chen, S.W., Synth. Commun., 1994, 24, 1339.
 - d). Bao, W.L., Zhang, Y.M., Synth. Commun., 1995, 25, 143.
 - e). Bao, W.L., Zhang, Y.M., Synth. Commun., 1995, 25, 1913.
- Katritzky, A.R., Kuzmierkiewicz, W., Rachwal, B., Rachwal, S., and Thomson, J., J. Chem. Soc. Perkin Trans. 1, 1987, 811.
- 5. a). Katritzky, A.R., Rachwal, S., Hitchings ,G.J., *Tetrahedron*, 1991, 47, 2683.
 b). Katritzky, A.R., Lan, X., Fan, W.Q., *Synthesis*, 1994, 445.

(Received in the UK March 7, 1996)