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

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

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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 SmI_2.

Diorganyl selenides and diorganyl tellurides are important organoselenium and tellurium compounds[1]. Furthermore, some other selenium and tellurium compounds, such as triorganyl selenonium halides, diorganyl tellurium dihalides, can be synthesized from diorganyl selenides and diorganyl tellurides[2]. It has recently been found that selenolate anion ($RSeSmI_2$) and tellurolate anion ($RTeSmI_2$) obtained from reductive cleavage of diorganyl selenides and tellurides with samarium diiodide are powerful nucleophilic reagents. Some interesting reaction have taken place with them[3]. The most interesting reactions caused by $RSeSmI_2$ or $RTeSmI_2$ 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:

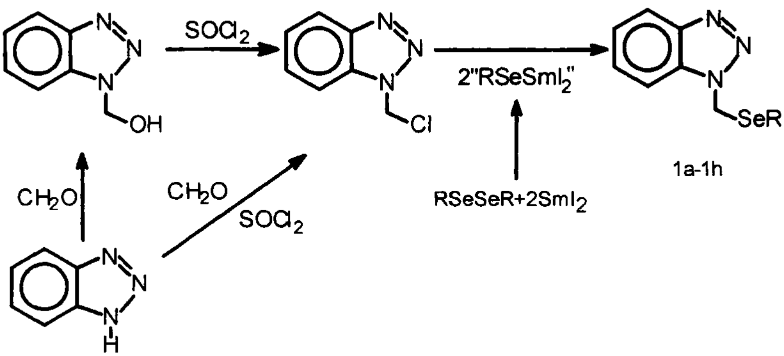
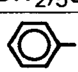
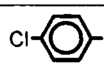
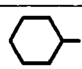


Table 1 1-(Benzotriazol-1-yl) Selenides

Entry	R	m.p. (℃)	Reaction Time(h)	Yield (%)
1a	CH_2CH_3	49-51	6	80
1b	$CH_2CH(CH_3)CH_3$	68-70	6	78
1c	$(CH_2)_3CH_3$	oil	6	82
1d	$(CH_2)_4CH_3$	oil	6	81
1e	$(CH_2)_5CH_3$	oil	6	80
1f		86-88	8	75
1g		110-112	8	72
1h		66-68	8	76

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

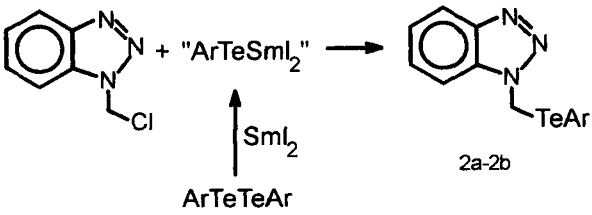
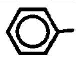
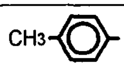


Table 2 1-(Benzotriazol-1-yl) Tellurides

Entry	R	m.p.(℃)	Reaction Time(h)	Yield (%)
2a		123-125	5	80
2b		112-114	5	83

The reactions were carried out at room temperatures. The starting material are easy to prepare[4]. 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 nucleophiles[5].

EXPERIMENTAL

^{1}H-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. SmI_2 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($CDCl_3$): 1.33(t, 3H, CH_3, J=6.8Hz), 2.62(q, 2H, $SeCH_2$, J=6.8Hz), 5.78(s, 2H, NCH_2), 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($CDCl_3$): 0.89(d, 6H, CH_3, J=6.6Hz), 1.23-1.77(m, 1H), 2.57(d, 2H, $SeCH_2$, J=7.2Hz), 5.77(s, 2H, NCH_2), 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(CCl_4): 0.87(t, 3H, CH_3, J=6Hz), 1.18-1.72(m, 4H), 2.59(t, 2H, $SeCH_2$, J=6.6Hz), 5.72(s, 2H, NCH_2), 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}.

1d: ^1H NMR(CCl_4): 0.84(t, 3H, CH_3, J=5.6Hz), 1.13-1.73(m,6H), 2.58(t, 2H, $SeCH_2$, J=6.2Hz), 5.73(s, 2H, NCH_2), 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: ^{1}H NMR(CCl_4): 0.80-1.71(m, 11H), 2.60(t, 2H, $SeCH_2$, J=6.2Hz), 5.72(s, 2H, NCH_2), 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: ^{1}H NMR($CDCl_3$): 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}.

1g: ^{1}H NMR($CDCl_3$): 5.96(s, 2H, NCH_2), 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: ^{1}H NMR($CDCl_3$): 1.43(m, 10H), 2.86-3.13(m, 1H), 5.85(s, 2H, NCH_2), 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: ^{1}H NMR($CDCl_3$): 6.16(s, 2H, NCH_2), 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: ^{1}H NMR($CDCl_3$): 2.30(s, 3H, CH_3), 6.12(s, 2H, NCH_2), 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}.

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