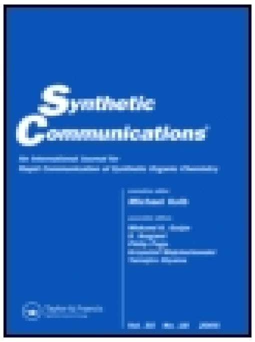


Synthetic Communications

ISSN: 0039-7911 (Print) 1532-2432 (Online) Journal homepage: http://www.tandfonline.com/loi/lsyc20

Synthesis of α-Benzotriazole Sulfides Promoted by Samarium Diiodide

Genliang Lu , Zhuangping Zhan & Yongmin Zhang

To cite this article: Genliang Lu , Zhuangping Zhan & Yongmin Zhang (1998) Synthesis of α-Benzotriazole Sulfides Promoted by Samarium Diiodide, Synthetic Communications, 28:19, 3657-3663, DOI: 10.1080/00397919808004912

To link to this article: http://dx.doi.org/10.1080/00397919808004912

SYNTHETIC COMMUNICATIONS, 28(19), 3657-3663 (1998)

SYNTHESIS OF α-BENZOTRIAZOLE SULFIDES PROMOTED BY SAMARIUM DIIODIDE

Genliang Lu, Zhuangping Zhan, and Yongmin Zhang*

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

Abstract: 1-(Benzotriazol-1-yl) unsymmetrical diorganyl sulfides were synthesized via replacement of chlorine atom in 1-(benzotriazol-1-yl)-1-chloromethane with thiolate anions promoted by SmI_2.

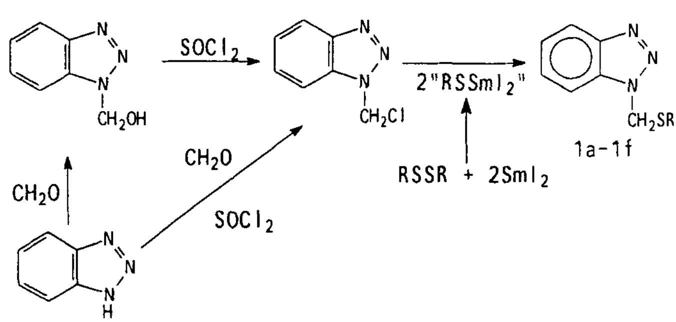
Benzotriazole methodology has already come a long way, but in the last decade benzotriazole was identified as an excellent synthetic auxiliary in many useful synthetic transformations.[1-4] α-Benzotriazole sulfides are useful synthetic intermediates. For example, tert-alkyl sulfides are conveniently prepared from α-benzotriazole sulfides by displacement of the benzotriazole group with Grignard reagents.[5] Vinyl sulfides are easily prepared from α-benzotriazole sulfides.[6] Some methods have been reported for prepration of α-benzotriazole sulfides. for examples, the reaction of thioles with 1-(chloromethyl) benzotriazole,[7] the

* To whom the correspondence should be addressed

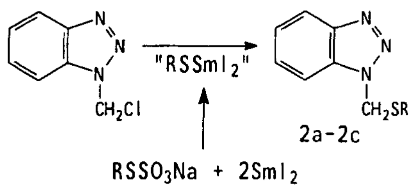
reaction of benzotriazole with aldehydes or ketones and thiols,[5] etc. However, those methods are suffered from using of metallic sodium, alkaline medium, and even low yield.

Samarium diiodide has been extensively applied to organic synthesis.[8-11] It has recently been found that thiolate anions($RSSmI_2$) obtained from reductive cleavage of diorganyl disulfides or sodium alkylthiolates with samarium diiodide are powerful nucleophilic reagents, and some interesting reations have taken place with them.[12] Here we wish to report that these alkylthiolate or arylthiolate 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 sulfides.

In view of the easy availablility of the starting materials,[13] good yields, simple operation, mild and neutral reaction conditions, we think that the present procedure provides a useful method for prepration of α-benzotriazole sulfides.



Scheme 1



Scheme 2

Table 1. Reaction Conditions and Yield of Products

Entry	R	Reation Time(h)	Yield* (%)
1a	$C_6H_5CH_2$-	14	84
1b	n-$C_{12}H_{25}$-	14	88
1c	n-$C_{16}H_{33}$-	14	82
1d	C_6H_5-	14	88
1e	p-ClC_6H_5-	12	88
1f	p-$CH_3C_6H_5$-	12	92
2a	$C_6H_5CH_2$-	16	72
2b	n-$C_{12}H_{33}$-	16	76
2c	n-$C_{16}H_{33}$-	16	70

* Yield of isolated Product.

Experimental Section

Melting points were uncorrected. HMPA was dried by CaH_2 and was then distilled in vacuo. 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 Bruker 80 spectrometer in $CDCl_3$ solution using

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

General Procedure

1. To a solution of SmI_2 (2.2mmol, in 22mL THF), 1mL HMPA[14] and 1mmol disulfide are added. After stirring for 1hr at 40°C, 2mmol of 1-(benzotriazol-1-yl) chloromethane is added. After stirring for the given hours at room temperatures (see table 1), the reaction mixture is treated with dilute hydrochloric acid (0.1M, 5mL) and extracted twice with ether. The combined organic layers are washed with saturated sodium thiosulfate solution (20 mL) and brine (20 mL). After the solution is dried over anhydrous $MgSO_4$, the solvents are removed under reduced pressure. The residue is purified by preparative TLC (silica gel) with cyclohexane and ethyl acetate (8:1) as eluent.

2. Sodium alkyl thiosulfate (1mmol) is added to the deep blue solution of SmI_2 (2.2mmol) in THF (22mL) at 70°C. The solution turned yellow within 20-30 min. and then was allowed to cool to room temperature. 1mmol of 1-(benzotriazol-1-yl) chloromethane is added and the mixture is stirred for 16 hrs. The reaction mixture is treated twice with ether. The combined organic layers are washed with saturated sodium thiosulfate solution (20 mL) and brine (20 mL). After the solution is dried over anhydrous $MgSO_4$, the solvents are removed under reduced pressure. The residue is purified by preparative TLC (silica gel) with cyclohexane and ethyl acetate (8:1) as eluent.

1a(2a)[7], m.p. 106-108°C (lit, 108-109°C) ; ^{1}H NMR, 8.2-8.0 (1H, m) , 7.7-7.2 (8H, m) , 5.65 (2H, s) , 3.70 (2H, s) ppm; IR, 3100, 3080, 3050, 3000, 2950, 1625, 1610, 1500, 1470, 1440, 1423, 1400, 1312, 1300, 1290, 1270, 1250, 1241, 1238, 1163, 1130, 1083, 1070, 1030, 1000, 936, 905, 778, 762 , 743, 709, 696, cm^{-1}.

1b(2b), m.p. 60-61°C; ^{1}H NMR, 8.1-7.9 (1H, m) , 7.6-7.2 (3H, m) , 5.58 (2H, s), 2.60-2.30 (2H, t) , 1.7-0.8 (23H, m) ppm; IR, 3085, 3060, 2998, 2940, 2862, 1626, 1602, 1503, 1475, 1460, 1435, 1380, 1300, 1270, 1225, 1160, 1090, 1078, 1025, 930, 885, 778, 760, 742, 720, 658, 600,cm^{-1}. Anal. Cacld. for $C_{19}H_{31}N_3S$: C, 68.41; H, 9.37; N, 12.60; Found: C, 68.35; H, 9.50; N, 12.50.

1c(2c), m.p. 70-72°; ^{1}H NMR, 8.1-7.8 (1H, m) , 7.6-7.2 (3H, m) , 5.67 (2H,s), 2.54-2.20 (2H, t) , 1.6-0.8 (31H, m) ppm; IR, 3080, 3040, 2995, 2925, 2860, 1620, 1600, 1500, 1490, 1470, 1458, 1430, 1398, 1310, 1299, 1265, 1250, 1220, 1158, 1100, 1080, 1050, 1020, 995, 940, 925, 880, 775, 755, 740, 715, 655, 600,cm^{-1}. Anal.Cacld. for $C_{23}H_{39}N_3S$: C, 70.90; H, 10.09; N, 10.78; Found: C, 70.78; H, 10.23; N, 10.85.

1d[7], m.p. 78-80°C (lit, 80°C) ; ^{1}H NMR, 8.2-8.0 (1H, m) , 7.6-7.3 (8H, m) , 5.98 (2H, s) ppm; IR, 3115, 3090, 3070, 3050, 3010, 2960, 1625, 1618, 1600, 1590, 1500, 1492, 460, 1448, 1440, 1400, 1318, 1290, 1268, 1240, 1230, 1160, 1132, 1082, 1070, 1025, 1000, 930, 852, 775, 762, 748, 732, 708, 682, 660, 600, cm^{-1}.

Synthetic Communications 1998.28:3657-3663.

1e, m.p. 104-106°C; ^{1}H NMR, 8.2-8.0 (1H, m) ,7.5-7.0 (7H, m) , 5.95 (2H, s) ppm; IR, 3080, 3040, 3015, 2945, 1625, 1600, 1502, 1485, 1460, 1425, 1398, 1392, 1310, 1298, 1285, 1265, 1250, 1240, 1230, 1170, 1138, 1120, 1100, 1070, 1010, 1000, 930, 880, 810, 778, 763, 750, 740, cm^{-1}. Anal. Calcd. for $C_{13}H_{10}ClN_3S$: C, 56.62; H, 3.66; N, 15.24; Found: C, 56.47; H, 3.61 N, 15.15.

1f[6], m.p. 102-104°C (lit, 101-103°C) ; ^{1}H NMR, 8.3-8.0 (1H, m) , 7.5-7.1 (7H, m) , 5.95 (2H, s) , 2.35 (3H, s) ppm; IR, 3080, 3060, 3040, 3020, 2950, 2940, 2875, 1625, 1600, 1502, 1460, 1430, 1422, 1400, 1390, 1320, 1310, 1298, 1282, 1265, 1250, 1240, 1230, 1187, 1160, 1140, 1135, 1090, 1075, 1020, 1000, 940, 930, 885, 800, 780, 750, 740, 710, 655, 600, cm^{-1}.

Acknowledgement

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

References

1. Katritzky, A.R.; Rachwal, S.; Hitchings, G.J. *Tetrahedron*, 1991, 47, 2683;
2. Katritzky, A.R.; Yang, Z.; Cundy, D.J. *Aldrichimica Acta*, 1994,27,31;
3. Katritzky, A.R..; Lan, X. *Chem. Soc. Rev.*, 1994, 363;
4. Katritzky, A.R..; Lan, X.; Fan, W.Q. *Synthesis*, 1994, 445;

5. Katritzky, A.R..; Perumal, S.; Kuzmierkiewiez, W.; Lue, P.; Greenhill, J.V. *Helvetica Chimica Acta*, 1991, 1924;

6. Katritzky, A.R..; Afridi, A.S.; Kuzmierkiewiez, W. *Helvetica Chimica Acta*, 1991, 1931;

7. Katritzky, A.R..; Rachwal, S.; Caster, K.C. *J. Chem. Soc., Perkin Trans. I*, 1987,781;

8. Girard. P.; Namy, J.L.: Kangan, H.B. *J. Am.Chem. Soc.*, 1980, 102, 2693;

9. Soderquist, J.A. *Aldrichimica Acta*, 1991,15;

10. Molender, G.A. *Chem. Rev.*, 1992, 92, 29;

11. Molender, G.A.; Harris, C.R. *Chem. Rev.*, 1996, 96, 307;

12. Jia, X.S.; Zhang, Y.M.; Zhou,X.J. *Synth. Commun.*, 1994, 24, 387;

13. Katritzky, A.R.; Kuzmierkiewiez, W.; Rachwal, B.; Thomson, I.. *J. Chem. Soc., Perkin Trans. I.*, 1987, 811.

14. HMPA is a highly toxic cancer suspect agent. (*Aldrich*, Catalog Handbook of Fine Chemicals 1996-1997.)

(RECEIVED IN THE U.S.A. 22 APRIL 1998)