SHORT PAPER

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Samarium diiodide mediated reductive addition reaction of 1-(phenylsulfonylmethyl) benzotriazole and 1-(benzoyloxymethyl) benzotriazole to aldehydes and ketones

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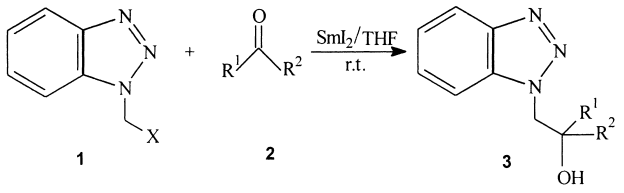
1-(β-hydroxyalkyl) benzotriazoles were prepared via reductive addition reactions of $Bt^1CH_2SO_2Ph$ or $Bt^1CH_2OC(O)Ph$ with aldehydes and ketones under mild conditions promoted by SmI_2.

Keywords: samarum diiodide, 1-(β-hydroxyalkyl) benzotriazoles

Benzotriazole is a synthetic auxiliary which has been used in a number of transformations, in recent years.[1] The Benzotriazole anion is a good leaving group, which has been used in place of a halogen atom in many reactions. A variety of compounds have been synthesised via a benzotriazole auxiliary, including, amines,[2] enamines,[3] esters,[4] ethers,[5] sulfides,[6] sulfones,[7] phosphorous-containing compopunds,[8] and selenium containing compounds.[9] Among numerous *N*-derivatives of benzotriazole, 1-(chloromethyl) benzotriazole has been studied in detail.[10, 11] Little attention has been paid to 1-(phenylsulfonylmethyl) benzotriazole and 1-(benzoyloxymethyl) in organic synthesis. Herein we wish to report that with SmI_2–Barbier protocol, $Bt^1CH_2SO_2Ph$ or $Bt^1CH_2OC(O)Ph$ **(1)** undergo reductive addition reactions smoothly with aldehydes and ketones **(2)** to give 1-(β-hydroxyalkyl) benzotriazoles **(3)** in good yields (Scheme 1).



X = $PhSO_2$, PhC(O)O

Scheme 1

Samarium diiodide has been wildly applied in organic synthesis as a powerful, versatile and ether-soluble one-electron transfer reductant.[12] Previous work has shown that SmI_2 can induce reductive debenzoyloxylation[13] and desulfonylation[14] successfully. However, little attention has paid to the reductive addition reactions following debenzoyloxylation and desulfonylation.[15] We found that $Bt^1CH_2SO_2Ph$ and $Bt^1CHOC(O)Ph$ could undergo reductive addition to aldehydes and ketones promoted by SmI_2 smoothly affording 1-β-(hydroxyalkyl) benzotriazoles in good yields. The results and scope of this reaction are shown in Table 1.

Thus, 1-β-(hydroxyalkyl) benzotriazoles were obtained under mild conditions. These products are useful in the synthesis of some oxygen-containing heterocylic compounds.[15] Literature strategies for the preparation of oxygen-containing heterocylic compounds include the subsequent reactions of lithiated 1-alkylbenzotriazoles[16] and 1-(α-trimethylsily) alkyl benzotriazoles.[17] The present method, however, requires only very mild conditions, thus may have more important utility.

In conclusion, under SmI_2–Barbier conditions, $Bt^1CH_2SO_2Ph$ and $Bt^1CHOC(O)Ph$ can undergo reductive addition reactions with aldehydes and ketones to afford 1-β-(hydroxyalkyl) benzotriazoles.

Experimental section

Melting points were uncorrected. IR spectra were recorded on a Bruck Vector 22 spectrometer, ^1H NMR spectra were obtain with a Bruker AC 80 MHz spectrometer in CDCl3 solution using TMS as internal standard. Mass spectra were obtained on a HP 5989B mass spectrometer. Elemental analyses were performed on a Carlo Erba 1106 instrument. The reactions were performed in a Schlenk type glass apparatus under a nitrogen atmosphere. THF was freshly distilled from sodium-benzophenone ketyl prior to use.

General procedure for the synthesis of 1-β-(hydroxyalkyl)benzotriazoles: Under nitrogen atmosphere, $Bt^1CH_2SO_2Ph$ (1 mmol, 5ml THF) or $Bt^1CHOC(O)Ph$ (1 mmol, 1ml THF) added to a solution of SmI_2 (2-3 mmol) in THF (25 ml). Then the mixture was stirred at room temperature. After given times (Table 1), the reaction mixture was quenched with hydrochloric acid (2 mol/l, 2 ml), and extracted with ether (3×15 ml). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and the solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel (1:3 ethyl acetate/cyclohexane).

Compound **3a:** m.p. 68–70°C. ν_{max} (KBr)/cm^{-1}: 3360, 3080, 2980, 1650, 1610, 1465, 1440, 1280, 1230, 1170, 1150, 1100, 780, 750. δ_H (ppm) 8.01–8.04 (m, 1H), 7.26–7.48 (m, 3H), 4.30 (d, 2H, *J*=7.2Hz), 3.41–3.61 (m, 1H), 2.30 (br, 1H), 1.23–1.50 (m, 6H), 0.86–0.88 (t, 3H, *J*=6.6Hz). MS: m/z, 220 (M+1), 219 (M+), 201 (2.00), 77 (100). Anal. calcd. for $C_{12}H_{17}N_3O$: C 65.75, H 7.76, N 19.18. Found: C 65.70, H 7.75, N 19.14.

Compound **3b:** m.p. 60–62°C (lit.,[11] 60–61 °C). ν_{max} (KBr)/cm^{-1}: 3360, 3090, 2980, 1650, 1610, 1465, 1440, 1280, 1230, 1170, 1150, 1100, 780, 750. δ_H (ppm) 8.01–8.02 (m, 1H), 7.26–7.40 (m, 3H), 4.50 (d, 2H, *J*=7.2Hz), 4.10–4.20 (m, 1H), 2.32 (br, 1H), 1.23–1.70 (m, 4H), 0.88–0.90 (t, 3H, *J*=6.6Hz).

Compound **3c:** m.p. 83–84°C (lit.,[11] 85°C). ν_{max} (KBr)/cm^{-1}:3340, 3090, 2980, 1650, 1610, 1465, 1440, 1280, 1230, 1170, 1150, 1100, 780, 750. δ_H (ppm) 8.01–8.02 (m, 1H), 7.26–7.40 (m, 3H), 4.50 (d, 2H, *J*=7.2Hz), 4.20–4.30 (m, 1H), 2.32 (br, 1H), 1.80–1.85 (m, 1H), 1.41–1.50 (m, 2H), 0.90 (d, 6H, J=6.0Hz).

Compound **3d:** m.p. 113–114°C (lit.,[11] 114°C). ν_{max} (KBr)/cm^{-1}: 3480, 3080, 3000, 1635, 1600, 1465, 1390, 1205, 1170, 1085, 930, 785, 765, 740. δ_H (ppm) 8.01–8.02 (m, 1H), 7.42–7.61(m, 3H), 4.61 (s, 2H), 2.23 (br, 1H), 1.32 (s, 6H).

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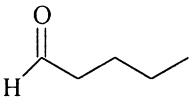
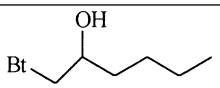
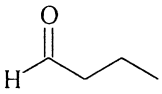
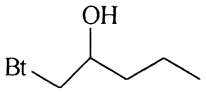
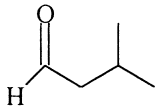
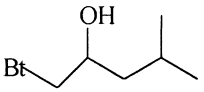
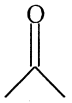
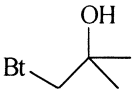
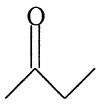
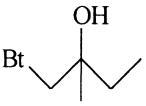
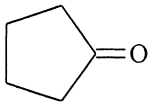
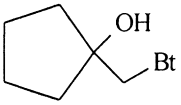
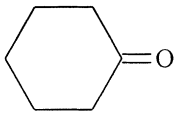
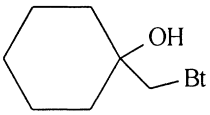
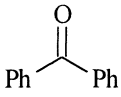
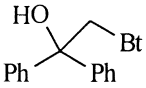
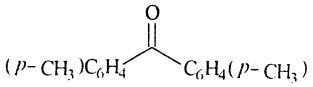
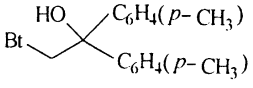
† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 1 Synthesis of 1-(β-hydroxyalkyl) benzotriazoles

Entry	X	SmI_2/mmol	Carbonyl compounds	Products	Time/h	Yield*/%
a	$PhSO_2$	3			4	85
	PhC(O)O	2			2	85
b	$PhSO_2$	3			4	80
	PhC(O)O	2			3	85
c	$PhSO_2$	3			4	75
	PhC(O)O	2			3	80
d	$PhSO_2$	3			4	75
	PhC(O)O	2			3	85
e	$PhSO_2$	3			4	80
	PhC(O)O	2			3	80
f	$PhSO_2$	3			4	75
	PhC(O)O	2			3	80
g	$PhSO_2$	3			4	75
	PhC(O)O	2			4	80
h	$PhSO_2$	3			4	85
	PhC(O)O	2			3	85
i	$PhSO_2$	3			4	80
	PhC(O)O	2			3	85

*Isolated yields

Compound **3e:** m.p. 110°C (lit.,[11] 110°C). ν_{max} (KBr)/cm^{-1}: 3460, 3080, 3000, 1645, 1620, 1465, 1395, 1350, 1240, 1200, 1095, 950, 780, 740. δ_H (ppm) 8.01–8.02 (m, 1H), 7.42–7.61(m, 3H), 4.61 (s, 2H), 2.23 (br, 1H), 1.55 (q, 2H, *J*=7Hz), 1.20 (s, 3H), 1.01 (t, 3H, *J*=7.5Hz).

Compound **3f:** m.p. 106-107°C (lit.,[11] 108°C). ν_{max} (KBr)/cm^{-1}: 3450, 3100, 2990, 1625, 1605, 1465, 1445, 1330, 1240, 1170, 1080, 1030, 940, 900, 780, 750. δ_H (ppm) 8.01–8.02 (m, 1H), 7.42-7.71(m, 3H), 4.71 (s, 2H), 2.40 (br, 1H), 1.40–1.81 (m, 8H).

Compound **3g:** m.p. 129–130°C (lit.,[11] 130°C). ν_{max} (KBr)/cm^{-1}: 3460, 3090, 2960, 1650, 1620, 1465, 1360, 1235, 1185, 1125, 1080, 1040, 990, 890, 780, 740. δ_H (ppm) 8.01–8.02 (m, 1H), 7.42-7.71(m, 3H), 4.63 (s, 2H), 2.40 (br, 1H), 1.40–1.80 (m, 10H).

Compound **3h:** 118–120°C (lit.,[11] 120°C). ν_{max} (KBr)/cm^{-1}: 3300, 3080, 3030, 2950, 1645, 1615, 1505, 1465, 1610, 1360, 1285, 1250, 1200, 1090, 1060, 945, 890, 780, 750, 700. δ_H (ppm) 7.90–8.10 (m, 1H), 7.10-7.71(m, 13H), 5.24 (s, 2H), 4.15 (s, 1H).

Compound **3i:** m.p. 109-110°C. ν_{max} (KBr)/cm^{-1}: 3310, 3090, 3040, 2950, 1645, 1620, 1505, 1465, 1360, 1285, 1250, 1200, 1090, 1060, 945, 830, 780, 740. δ_H (ppm) 7.93–7.95 (m, 1H), 7.04–7.38(m, 11H), 5.26 (s, 2H), 4.16 (s, 1H), 2.26 (s, 6H). MS: *m/z*, 344 (M++1), 326 (4.79), 119 (100). Anal. calcd. for $C_{22}H_{21}N_3O$: C 76.97, H 6.12, N 12.24. Found: C 76.95, H 6.10, N 12.22.

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