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NOTE

Capture of the Anions Derived from *n*- and *sec*-Butyl-1,2-benzisothiazole-1,1-dioxides by Iodomethane Using 1,8-Diazabicyclo-[5,4,0]-7-undecene

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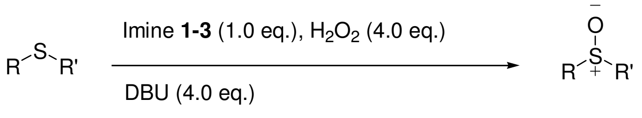
Deprotonation of primary and secondary alkyl 3-substituents of 3-alkyl-1,2-benzisothiazole-1,1-dioxides was confirmed by capture of the anions derived from the *n*- and *sec*-butyl compounds (**1** and **2**) using methyl iodide, giving modest yields of mixtures of the E- and Z-N-methyl 3-alkylidene derivatives **4** and **5**.

Key Words: Deprotonation, Butyl compounds, Iodomethane, 1,8-Diazabicyclo-[5,4,0]-7-undecene.

In earlier reports[1-3], it is shown that 3-substituted-1,2-benzisothiazole-1,1-dioxides derived from saccharin are able to catalyze, in sub-stoichiometric amounts, the oxidation of sulfides to sulfoxides under basic reaction conditions, as are certain other sulfonylimines[4,5]. Oxidation reactions were carried out by addition of a solution of hydrogen peroxide (4.0 equiv., 30 % w/v aqueous solution) to a cooled, stirred dichloromethane solution of 1,8-diazabicyclo-[5,4,0]-7-undecene (DBU) (4.0 equiv.), followed by sulfonylimine **1-3** (1.0 equiv.) (**Scheme-I**). The methyl *p*-tolyl sulfide substrate (1.0 equiv.) was then added and the reaction progress was monitored by TLC.



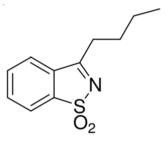
Scheme-I

Yields were generally low using DBU as base, except for the 3-*tert*-butyl derivative (**3**), which showed quantitative conversion and could be used in sub-stoichiometric quantities for oxidation of sulfides to sulfoxides (Table-1).

TABLE-1
OXIDATION OF METHYL *p*-TOLYL SULFIDE MEDIATED BY IMINES **1-3**

Entry	Mediator	R	Time	Temp. (ºC)	Yield (%)
1	1	Bu^n	2 h	25	7
2	3	Bu^t	2 h	25	100
3	3†	Bu^t	7 d	25	85†
4	2	Bu^s	2 h	20	5

†0.1 Molar equivalent of the mediator used.



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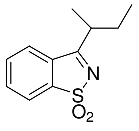

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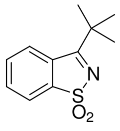
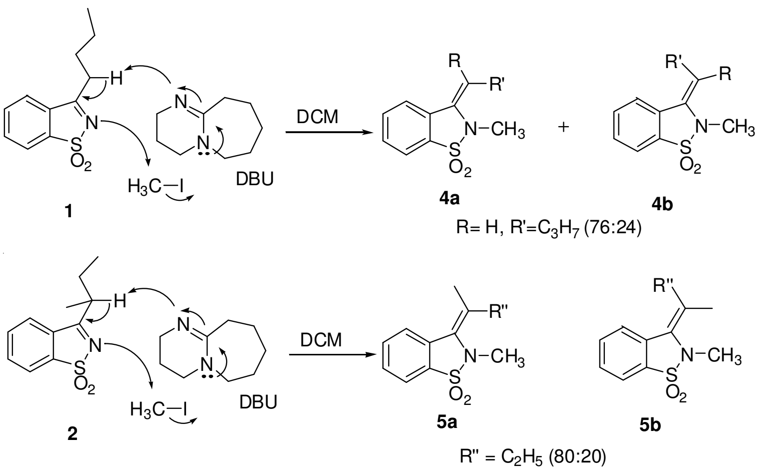


3

We have now shown the lower reactivity of **1** and **2** to be related to the acidity of α-proton of their primary and secondary alkyl substituents. Ready deprotonation of the primary and secondary alkyl-substituted mediators by DBU was confirmed by capture of the derived anions using methyl iodide (**Scheme-II**), giving modest yields of mixtures of the Z- and E- N-methyl-3-alkylidene derivatives **4** and **5** (*ca.* 76:24 % for the *n*-butyl derivative **4a-4b** and *ca.* 80:20 % for the *sec*-butyl compounds **5a-5b**, by nuclear Overhauser effect studies).



Scheme-II

Consistent with the proposed structures **4** and **5** is the lack due to no IR absorption at 1600-1560 cm^{-1} (C=N). However, IR absorptions at 1646, 938 cm^{-1} which can be related to C=C bond in the product and the appearance of sharp singlets at 3.0-3.3 ppm (N-methyl) and signals characteristic of vinyl protons at 5.5 ppm. Under the same reaction conditions, the 3-*tert*-butyl derivative of saccharin **3** was recovered unchanged at the end of reaction.

These reactions appear to provide evidence supporting our conjecture[1] that competing deprotonation processes are the cause of the relatively poor performance of catalysts **1** and **2** in sulfur oxidation reactions.

3-Butylene-N-methyl-1,2-benzisothiazole-1,1-dioxide (4): 3-*n*-Butyl-1,2-benzisothiazole-1,1-dioxide (**1**) (223 mg, 1.0 mmol) and DBU (152 mg, 1.0 mmol) were added to dichloromethane (10 mL). After stirring for 0.5 h, iodomethane (0.5 mL, 8.03 mmol) was added dropwise and the reaction mixture stirred for 23 h. Ether (30 mL) and water (30 mL) were added and the organic layer washed with water (2 × 30 mL) and dried over anhydrous $MgSO_4$. Removal of the solvents *in vacuo* gave the crude product as a solid, which was purified by flash column chromatography (ether-*n*-pentane, 1:1) to give a colourless solid (83 mg, 35 %). ^1H NMR spectroscopy indicated the presence of a 24:76 ratio of E and Z- methyl-1,2-alkylidenes, determined by integration of the singlets ($N-CH_3$) appearing at 3.1 and 3.3 ppm, m.p. 87-90 °C (from EtOH); (Found: C, 60.53; H, 6.40; N, 5.86. $C_{12}H_{15}NO_2S$ requires C, 60.73; H, 6.37; N, 5.90 %); ν_{max} (nujol)/cm^{-1} 1658, 929 (C=C) 1377 and 1164 (SO_2); δ_H (300 MHz; $CDCl_3$) 1.0 (3 H, t, *J* = 7, CH_3), 1.6 (2 H, m, *J* = 8, CH_2CH_3), 2.4 (2 H, q, *J* = 8 $CH_2CH_2CH_3$), 3.1 (3H, s, $N-CH_3$), 3.3 (3 H, s, $N-CH_3$), 5.0 (1H, t, *J* = 8, CH), 5.5 (1 H, t, *J* = 7, CH) and 7.4-7.9 (4 H, m, Ar); δ_C (300 MHz; $CDCl_3$) 13.8, 23.6, 26.0, 28.6, 29.3, 31.0, 107.6, 108.5, 120.5, 121.1, 124.9, 129.2, 129.3 and 132.9; m/z (EI) 237 (M^+, 12 %) and 208 (100).

3-*sec*-Butylene-N-methyl-1,2-benzisothiazole-1,1-dioxide (5): 3-*sec*-Butyl-1,2-benzisothiazole-1,1-dioxide (**1**) (223 mg, 1.0 mmol) and DBU (152 mg, 1.0 mmol) were added to dichloromethane (10 mL). After stirring for 0.5 h, iodomethane (0.5 mL, 8.03 mmol) was added dropwise and the reaction mixture stirred for 23 h. Ether (30 mL) and water (30 mL) were added and the organic layer washed with water (2 × 30 mL) and dried over anhydrous $MgSO_4$. Removal of the solvents *in vacuo* gave the crude product as a solid, which was purified by flash column chromatography (ether-*n*-pentane, 1:1) to give a pale yellow oil (27 mg, 11 %). ^1H NMR spectroscopy indicated the presence of a 20:80 ratio of E and Z-methyl-1,2-alkylidenes, determined by integration of the singlets ($N-CH_3$) appearing at 2.9 and 3.4 ppm, (Found: C, 61.21; H, 6.78; N, 5.83. $C_{12}H_{15}NO_2S$ requires C, 60.73; H, 6.37; N, 5.90 %); ν_{max} (nujol)/cm^{-1} 1646, 938 (C=C), 1377 and 1172 (SO_2); δ_H (300 MHz; $CDCl_3$) 1.2 (3 H, t, *J* = 8, CH_2CH_3), 2.1 (3 H, s, CCH_3), 2.5 (2 H, q, *J* = 8, CH_2), 2.9 (3 H, s, $N-CH_3$), 3.9 (3H, s, $N-CH_3$) and 7.4-7.8 (4 H, m, Ar); δ_C (300 MHz; $CDCl_3$) 12.0, 12.2, 17.9, 20.6, 26.9, 29.2, 38.3, 39.5, 76.6, 77.0, 77.4, 121.6, 121.7, 124.7, 125.3, 128.3, 128.4, 132.2, 132.4, 132.7, 135.3, 135.6, 135.7, 136.0 and 136.1; m/z (EI) 237 (M^+, 35%) and 222 (100).

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