Molbank **2010**, M648

OPEN ACCESS

molbank

ISSN 1422-8599

www.mdpi.com/journal/molbank

Short Note

3-Methyl-4,5,6,7-tetrahydro-1-benzothiophene-2-carboxylic Acid

Sembian Ruso Jayaraman [1,*], Madhavan Sridharan [1] and Rajendiran Nagappan [2]

[1] Syngene Intl. Ltd., Biocon Park, Plot No.2&3, Bommasandra IV phase, Jigani Link Road, Bangalore-560 099, India

[2] Department of Polymer Chemistry, University of Madras, Gundy Campus, Chennai-600 025, India

* Author to whom correspondence should be addressed; E-Mail: Sembian.Ruso@syngeneintl.com; Tel.: +919880455664, 9180 2808 2808.

Received: 01 December 2009 / Accepted: 24 December 2009 / Published: 6 January 2010

Abstract: 3-Methyl-4,5,6,7-tetrahydro-1-benzothiophene-2-carboxylic acid was synthesized chemoselectively from 3-formyl-4,5,6,7-tetrahydro-1-benzothiophene-2-carboxylic acid, using Et_3SiH/I_2 as a reducing agent. The title compound was characterized by IR, ^{1}H NMR, ^{13}C NMR and LCMS.

Keywords: triethylsilane; iodine; 3-formyl-4,5,6,7-tetrahydro-1-benzothiophene

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1. Introduction

In recent years, the popularity and usage of silicon reagents have tremendously increased due to their stereoselectivity [1] and chemoselectivity [2]. The reductive halogenations of carbonyl compounds were promoted by silicon hydride under the influence of trimethyl or tetramethyl [3,4] silyl-based reagents, providing a way to form benzyl halides. The reduction of alcohols [5] and aromatic ketones [6] to their corresponding hydrocarbons were carried out using triethylsilane and an acid or Lewis acid catalyst.

Various conversions and syntheses were carried out using Et_3SiH/I_2 as a reagent, such as hydroiodination of alkenes and alkynes, preparation of 3,6-dihydropyrans from glycals, *etc*. [7–10].

An exploratory vision of interest on sulphur-containing heterocycles is due to their potential antimicrobial activity [11–13]. At present, we are reporting the facile conversion of 3-formyl-4,5,6,7-

tetrahydro-1-benzothiophene-2-carboxylic acid to 3-methyl-4,5,6,7-tetrahydro-1-benzothiophene-2-carboxylic acid, using easily available Et_3SiH/I_2 as a reducing agent.

2. Result and Discussions

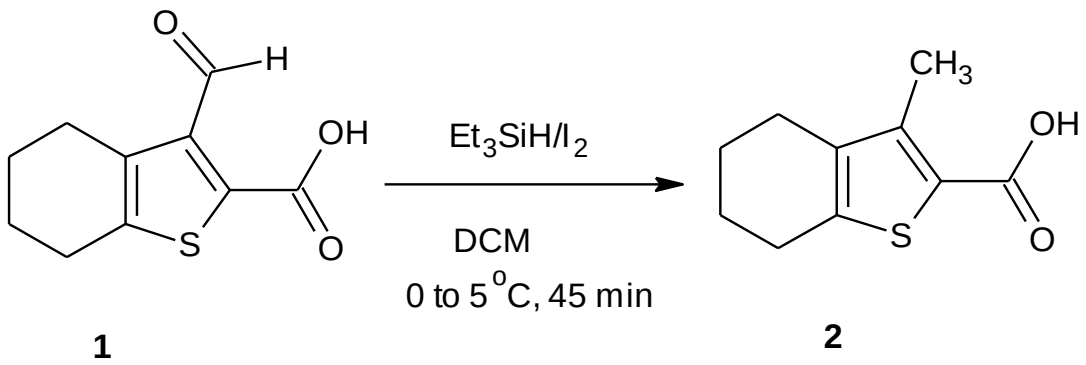
A synthesis of 3-methyl-4,5,6,7-tetrahydro-1-benzothiophene-2-carboxylic acid is reported from 3-formyl-4,5,6,7-tetrahydro-1-benzothiophene-2-carboxylic acid via chemoselective reduction using Et_3SiH/I_2 as a reducing agent. The transformation of the formyl group (compound **1**) into a methyl group (compound **2**) was clearly established on the basis of IR, ^{1}H, ^{13}C NMR and mass spectral data.

^{1}H NMR: The aldehyde proton was not appearing in compound **2** and the proton signal at 2.41 ppm for three protons as a singlet indicates the presence of methyl group which was formed from the formyl group by reduction.

^{13}C NMR: The signal at 168.73 ppm indicates the carbonyl carbon of the acid and the signal at 13.58 ppm is assigned to the methyl carbon.

All the spectral details of compound **2** are disclosed in the experimental part.

Scheme 1. Conversion of 3-formyl-4,5,6,7-tetrahydro-1-benzothiophene-2-carboxylic acid into 3-methyl-4,5,6,7-tetrahydro-1-benzothiophene-2-carboxylic acid.



3. Experimental

3-Methyl-4,5,6,7-tetrahydro-1-benzothiophene-2-carboxylic acid (**2**)

Iodine (12 g, 0.048 mol, 1 eq) was added portionwise to a stirred, ice-cooled mixture of 3-formyl-4,5,6,7-tetrahydro-1-benzothiophene-2-carboxylic acid (10 g, 0.048 mol, 1 eq) and triethylsilane (15.15 mL, 0.095 mol, 2 eq) in DCM (100 mL). The reaction mixture was stirred at 0 to 5 °C for 10 min and then at RT for 45 min. It was then diluted with DCM (100 mL) and quenched with an aqueous solution of sodium bisulphate (50 mL, 20%). The organic layer was separated and washed with HCl (100 mL, 0.5 N), washed with water (100 mL) and brine, dried over sodium sulphate and concentrated to give 10 g of a yellow solid. The crude product was recrystallised from ethyl acetate to afford 7.5 g of a pale yellow solid, 80% yield.

Melting point: 219.8–221.6 °C.

MS (EI): M-1 (m/z) = 195.

IR (cm^{-1}): 1638 (C=O), 1276 (C-O, strong), 2932, 2836 (CH_3-C), 2193, 2169 (C-H, aliphatic).

^{1}H NMR (400 MHz, $CDCl_3$): δ/ppm 1.82–1.85 (m, 4H), 2.41 (s, 3H), 2.48–2.50 (t, 2H), 2.77–2.79 (t, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ/ppm 168.73 (C=O), 146.84, 144.08, 137.38, 122.31 (aromatic carbon), 25.54, 24.38, 22.90, 22.21, 13.62 (methyl carbon).

Elemental analysis: Calculated for $C_{10}H_{12}O_2S$: C, 61.22; H, 6.12; S, 16.32. Found: C, 60.86; H, 5.96; S, 16.16.

Acknowledgements

The authors thank Syngene Intl. Ltd. Bangalore, India for providing the facilities to carry out the research work.

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